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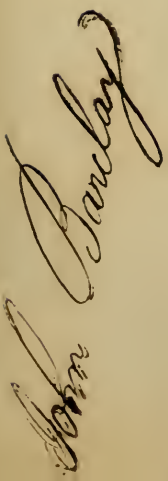
A MANUAL

OF THE

ART OF DYEING.



IN ACTIVE PREPARATION,

A MANUAL OF

DYEING RECEIPTS,

FOR GENERAL USE.

BY JAMES NAPIER, F.C.S.

WITH NUMEROUS SAMPLES OF DYED CLOTH.

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NO. CO

A MANUAL

OF THE

ART OF DYEING.

BY

JAMES NAPIER, F.C.S.

ILLUSTRATED BY ENGRAVINGS.

GLASGOW:
PUBLISHED BY RICHARD GRIFFIN & COMPANY.
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1853.

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PREFACE.

If there be any trade which, more than another, requires the knowledge of first principles, it is that of dyeing, it being essentially progressive. The particular conditions of the trade render information of this description more needful, and therefore more valuable, than ordinary. The trade is what is termed open, so that any man may enter it; and, in consequence, there are few instances where young men are taught the business systematically. A great many enter the trade who are grown up,—their chief ambition being to learn the mechanical operations of the dye-house, and when sufficient dexterity in these is attained, to secure the highest rate of wages. When this is accomplished, zeal for improvement in a great measure subsides. However, there are many who, not content with acquiring a knowledge of the mere mechanical routine, desire to look deeper into the principles of the art, and aim at higher honours than those of a mere labourer in it, but who believe that the means of success consist simply in long and steady service, and a good memory for the rules of manipulation. Both of these are valuable qualifications, but neither of them would be depreciated in the slightest degree by being conjoined with a more extended knowledge of the fundamental principles of the art than usually falls to the share of the practical dyer. There is another evil arising out of this condition of

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the trade. Individuals who attain the position of good workmen value their abilities by the contrast which exists between them and the newly-initiated journeyman; but they rarely or never look forward to the wide field which lies unexplored before them. Often indeed they boast of their capabilities, of their expertness, and their knowledge; and it is no uncommon thing for them to indulge in petty jealousy, and endeavour to conceal the *secret* of their mode of working from their neighbours. Under these circumstances it is no wonder that years are often spent—we should say wasted—in endeavouring to discover what was long before patent to every one who knew the scientific principles of the trade, although ignorant of the practical operations of it. This ignorance of principles often makes both workman and master the dupes of knaves who go about hawking *valuable secrets* at so much a piece.

It must be admitted, however, that notwithstanding all untoward circumstances, the degree of advancement which the art has attained is truly astonishing. A single practical hint is sometimes sufficient to cause a complete revolution in some branch of the trade, so that were the principles of chemistry in their application to dyeing but once generally understood by those practically employed, we can hardly conceive what changes and improvements might not be effected.

Another circumstance calling for a few remarks is the fluctuating state of the trade, which, even in its best condition, throws not less than a fourth part of the workmen idle during the winter months. But while we admit the hardship of such a state of things in its fullest extent, we do not believe that this time should be allowed to glide by in absolute listlessness. It is still a portion of the allotted span of life, and ought to be turned to all the advantage which circumstances will admit; and if it can be made subservient to future advantage either by advancing the personal interests, or in augmenting the mental enjoyment, of the individual, it is surely

culpable to allow it to run to waste. We sincerely believe that it may be turned to account in both ways, and we promise with some confidence that the following Treatise will suggest the means of deriving remuneration even from idle hours. Lord Bacon's maxim, that "Knowledge is power," has been reiterated till it may be thought to have lost its virtue, but it is still as true as ever, and we are confident that it cannot be more aptly applied than to the case of the practical dyer.

From our own experience we are aware that there at present exists a strong desire amongst a great many of those employed in the processes of dyeing to understand the principles of the art, and to be able to assign reasons for the various changes that take place in producing the colours. Such knowledge is often eagerly sought for without success, both in books and in the lecture-room. The disappointment arises from two sources: first, the inability of the dyer to apply chemical principles to his special purposes; and second, a want of practical knowledge in the author or lecturer, which disqualifies him for pointing out the special applications of the principles he may be defining. These circumstances have long impressed the Author with the opinion that an application of principles to any practical operation can best be done by an individual working at, or familiar with, all the practical details of that particular operation or trade, and that every branch of trade or art ought to have its own guide-book prepared by one of its own operatives. The carrying out of this idea has induced the Author to publish the present MANUAL, which is a "SYSTEM OF CHEMISTRY APPLIED TO DYEING." Having been himself a practical dyer for many years, and having experienced the difficulties which an uneducated man has to contend with in striving to become a Dyer in the proper sense of the term, he has in the following pages endeavoured to clear away some of the technical difficulties besetting the path of the practical man, and to guide him in

following out first principles while engaged in experiments to advance his art.

The Author acknowledges his obligations to a few intelligent dyers for several practical hints contained in these pages, and which had not come under his own observation. It will also be seen in reading the work, that advantage has been taken of some valuable articles in foreign journals, translations of some of which have appeared in chemical periodicals, such as the *Pharmaceutical Times*, which is now discontinued, and the *Chemical Gazette*, a journal which he earnestly recommends to the practical dyer, as containing from time to time papers of great value upon Dyeing and Dyestuffs.

Partick, Glasgow,
25*th Feb.*, 1853.

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DYEING.

GENERAL PROPERTIES OF MATTER.

HEAT.

Conditions of Matter.—Matter, which is every thing capable of affecting the senses, exists in three different states,—solid, fluid, and gaseous. Looking upon matter in any of these states, the most casual observer cannot fail to distinguish a great variety of appearance. For example,—stone differs from brick, bread from wood, and iron from both, among the solid forms; while differences quite as great are seen both in fluids and amongst gases. But, although these differences are familiar to all, there are few who inquire the cause why, under the same circumstances, one portion of matter exists as a solid, another as a fluid, and a third as a gas. Correct answers to these inquiries are the objects of all scientific research. They are, in their nature, twofold—*physical* and *chemical*. The former, embracing the study of matter in *mass*, takes cognizance of shape, measure, hardness, weight, flexibility, tenacity, divisibility, and such like properties; while the latter, the chemical, investigates those more remote differences which depend on the relative powers, properties, and mutual actions of the elemental components of the given substance—an inquiry which embraces a universal interrogation of all kinds of matter.

Heat the Cause of Conditions of Matter.—That one body is solid, another fluid, and a third gaseous, is an inquiry which belongs more directly to physics than to chemistry; yet heat, which is the cause of these differences, is so intimately connected both with the molecular changes, and the constitution of bodies, particularly of the colouring matters used in dyeing,

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that it will be proper to enumerate, preliminarily, a few of its most prominent effects and general laws, for convenience of frequent reference when we come to speak of the practical effects of those laws on many of the operations in the dye-house.

All bodies are supposed capable of existing in the three states—solid, fluid, and gaseous—by the addition or subtraction of heat; but the same degree of heat does not affect all kinds of bodies to the same extent. For example,—water, subject to the ordinary pressure of the atmosphere, at 32° Fah. and under, is solid, from 32° to 212° it is fluid, and from 212° upwards it is gaseous; while quicksilver, another fluid, at ordinary temperature, does not become solid until it is cooled 72° below that of the solidifying point of water, and does not pass into the gaseous state until it is heated upwards of 400° above the aeriform point of water. Again, lead and several other bodies only become fluid at the temperature which gasifies quicksilver. The following table will make this more apparent:—

	Solid matter	Becomes fluid at	Becomes gaseous at	Range of fluidity.
Sulphurous Acid,...	105	105	14	91
Carbonic Acid,.....	71	None.	71	None.
Mercury,.....	39	39	622	701
Water,.....	32	32	212	180
Tin, ...	442	442	about 2400	about 2058
Lead,.....	594	594	Not known.	
Bismuth, ...	500	500	900	400
Arsenic,.....	356	None.	356	None.
Silver, ...2283		2283	Not known.	
Cast Iron,.....3479		3479	Not known.	

This table shows how differently the same degree of heat affects different substances. We cannot conceive a condition *so cold* that all matter would be solid, nor *so hot* that all would be gaseous. In the cases of carbonic acid and arsenic, there appears an exception: these bodies have no fluid range —they have no existence in a fluid state. The former may be obtained fluid by pressure; but this is under extraordinary circumstances, and the particles still retain their elasticity, which a true fluid does not. But when in the solid state, and

under ordinary conditions—that is, under the ordinary pressure of the atmosphere—it passes directly from the solid to the gaseous state.

Some philosophers, reasoning from analogy, and not admitting any exceptions to general laws in nature, object to the apparent fact, and give, as their opinion, that such substances as carbonic acid really have a fluid range, but being so little, probably only a few degrees, the body may pass through that state without observation. This supposition is untenable, and is founded upon a mistaken view of what is a general law. The range of fluidity of any body depends upon the amount of pressure which the body is subject to. There are many other bodies, besides carbonic acid and arsenic, that require a greater amount of pressure than that of our atmosphere to maintain them in the fluid state; so that both the facts and the circumstances are quite in accordance with the general laws of nature.

General Effects of Heat.—In connection with the general laws of heat, we may notice, first, that bodies when they become heated expand, or become larger—the particles which compose them seem to separate farther from one another. This effect is produced upon matter in all states. Familiar illustrations of this effect of heat are numerous. If a pair of tongs, with legs of equal length, have one of the legs put into the fire and made red hot, it will be found, in this state, longer than the other. It is well known to dyers, that if a boiler be filled to within a little of the mouth with cold water, and a fire put under it, by the time it begins to boil the water runs over, having enlarged so much that the boiler is too small to contain it when hot. And another circumstance often occurs—when a certain quantity of a decoction of a dye is required, and is measured out of the boiler in gross while hot, and then distributed in its required proportions when cold, there is often wanting a considerable portion of liquid, causing serious annoyances in the dye-house, when the difference of temperature is not taken into consideration.

That gaseous bodies are affected in the same way by heat, may be illustrated by taking a bladder, and filling it three parts full with cold air, tying it round the neck, and holding it before a fire—or, what is better, taking the bladder into the drying-stove connected with the dye-house. In a very little

the bladder becomes distended and quite full, and may be made to burst by the expansion of the air, if the heat be high, or the bladder nearly filled.

Measures of Temperature.—Upon this expansive effect of heat is founded the means of measuring its intensity. Our senses tell us when a body is hot or cold, but they are very imperfect indicators of the degree or intensity of the heat. Our own temperature being the standard, we can only tell that a substance is hotter or colder than our own body. In the dye-house, where the hand is often made the indicator of the temperature of the dyeing liquid, the result varies according to whether the person has been previously working in hot or cold liquids, and is therefore a very imperfect test of temperature, and often productive of evils by giving different tints of shades, and deteriorating the beauty of a colour. Temperature is very correctly measured by observing the amount of expansion in any given body. Instruments for this purpose are plentiful and cheap: we will therefore not require to detail their mode of manufacture, but a good thermometer is an essential instrument in the dye-house, and ought to be constantly employed. The thermometers used in this country are generally those of Fahrenheit. The scale of measurement of this has been determined in the following manner:—Fahrenheit divided the two points, from the freezing of water to its boiling, into 180 degrees: he called the freezing point the 32d degree, from some reason of his own; hence $32° + 180° = 212$, the boiling point of water, according to Fahrenheit. There is another scale sometimes used, called Reaumur's. This has the two points, from the freezing to the boiling of water, divided into 80 degrees. Another, and more generally used scale, has the range from freezing point to boiling of water divided into 100°; thus the freezing point is marked 0, the boiling point 100. This is termed the Centigrade thermometer. In reading books where temperature is referred to—such as in many dyeing recipes and processes—attention must be paid which thermometer scale is referred to. They are generally indicated by abbreviations,—as F., or Fah., for Fahrenheit's scale, R., or Reau., for Reaumur's, and C. for the Centigrade. The following table of the comparative value of the different scales, will guide the operator in using one or other of them:—

Cent.	Fah.	Cent.	Fah.	Cent.	Fah.
0	32	34	93.2	68	154.4
1	33.8	35	95	69	156.2
2	35.6	36	96.8	70	158
3	37.4	37	98.6	71	159.8
4	39.2	38	100.4	72	161.6
5	41	39	102.2	73	163.4
6	42.8	40	104	74	165.2
7	44.6	41	105.8	75	167
8	46.4	42	107.6	76	168.8
9	48.2	43	109.4	77	170.6
10	50	44	111.2	78	172.4
11	51.8	45	113	79	174.2
12	53.6	46	114.8	80	176
13	55.4	47	116.6	81	177.8
14	57.2	48	118.4	82	179.6
15	59	49	120.2	83	181.4
16	60.8	50	122	84	183.2
17	62.6	51	123.8	85	185
18	64.4	52	125.6	86	186.8
19	66.2	53	127.4	87	188.6
20	68	54	129.2	88	190.4
21	69.8	55	131	89	192.2
22	71.6	56	132.8	90	194
23	73.4	57	134.6	91	195.8
24	75.2	58	136.4	92	197.6
25	77	59	138.2	93	199.4
26	78.8	60	140	94	201.2
27	80.6	61	141.8	95	203
28	82.4	62	143.6	96	204.8
29	84.2	63	145.4	97	206.6
30	86	64	147.2	98	208.4
31	87.8	65	149	99	210.2
32	89.6	66	150.8	100	212.0
33	91.4	67	152.6		

It will be seen from this table that every 5 degrees of the Centigrade scale is equal to 9 Fahrenheit; so that any degree of the one may be converted into the other by a simple rule, namely, by multiplying the Centigrade by 9, and dividing by 5, then adding 32°. Thus, if any liquid is recommended to be at 60° C., then 60° Cent. $\times$ 9 $\div$ 5 + 32° = 140° F.; or, by

Reaumur's, the only difference in the process is to divide by 4 instead of by 5. Thus, 60° R., × 9 ÷ 4 + 32° = 167° F.

Boiling of Liquids.—The heating and boiling of liquids is explainable by the principle of expansion. When heat is applied to a vessel holding water, the particles of water nearest the fire become heated, and consequently expand; and, in this expanded state, being lighter than the particles above them, they rise to the surface and give place to another layer of particles. These particles are in turn heated, and rise to the surface; and so on, successively, until the fluid is all heated to the point at which it passes off as vapour or steam. The exact temperature at which this takes place is stated above as 212° Fah., but varies a little from the amount of pressure upon its surface, so that water boils at a lower heat upon a high hill than at the foot of it; and, for the same reason, it requires a higher temperature to boil the water at the bottom of a deep pit than upon the surface at the mouth of the pit—there being a greater pressure of air at the bottom of the pit in proportion to the depth.

Substances Affecting Boiling Point.—Anything that gives an increased attraction to the particles of a fluid also raises the temperature of the boiling point. Some kinds of vessels—such as glass and polished metals—retain the water with greater force than rough vessels, hence it requires a little higher heat to boil water in vessels of polished material. Water, upon the surface of oil, boils two degrees of heat below water in a glass vessel, in consequence of the oil having no attraction for water.

Substances dissolved in water have often a similar effect, the attraction of the two substances having to be overcome. Thus, alkaline leys—soda or potash dissolved in water—require higher temperatures to boil them than pure water does. But, connected with this, we may mention a circumstance of great importance in the dye-house. In boiling alkaline leys, so strong is the attraction of the water for the alkali, that it carries a small quantity with it in passing off as steam; so that great care should be taken in a dye-house where leys are being boiled, that the steam or vapour does not come into contact with any colours that will be affected by alkalies. Where convenient, it is, indeed, safest to have all alkaline leys boiled entirely apart from where any coloured goods are likely to be

exposed to the influence of these vapours. We have seen many annoying and expensive accidents caused by neglecting this precaution, especially upon such colours as safflower reds and Prussian blues.

Strong Boiling.—Another circumstance of common occurrence in the dye-house is what is termed *strong boiling*. This means that, in the process of boiling, we increase the fire, in order to give the liquor more heat, and make it hotter. We need hardly say that this is an error; for a liquid at the boiling point cannot be more heated by increase of fire. All that is required is as much heat as will retain it on the *spring* of the boil, and the liquid will then be as hot as though it boiled with the greatest violence. The only difference in strong boiling is, that much more steam is driven off, which carries off the heat applied, and lessens the quantity of solution; still, if a thermometer be placed in the liquor, the temperature is found to be the same, and the only effect is that the heat is more rapidly carried off by the steam, and lost. The amount of heat which steam thus imbibes and takes away, is calculated, in round numbers, at 1000° Fah., which may be illustrated as follows:—If one pound of water, at 32°, requires the burning of a pound of coal to bring it to the boiling point, (212°) the water will have received 180° of heat; if the fire be continued at the same rate, it will take $5\frac{1}{2}$ lbs. of coal to convert the pound of boiling water into steam, and the temperature of the steam will never be above 212° Fah.: thus 1000° of heat have been taken up by the steam, and retained in a latent state,—that is to say, in a state not sensible to the thermometer. Or we may illustrate this principle by another experiment: if we take $5\frac{1}{2}$ lbs. of water at 32°, and pass a jet of steam at 212° through it, until the water begins to boil, the whole water will weigh $6\frac{1}{2}$ lbs.; thus 1 lb. of steam has brought $5\frac{1}{2}$ lbs. of water up 180°, thereby showing that this pound of steam had contained 1000° of heat. These facts the practical dyer can easily apply to his own purposes. Steam is very generally used in the dye-house as a heating agent for water, making decoctions, and the boiling of goods. It is an observed fact that steam is not so effective for many purposes as fire—as in the making of some decoctions. In the using of steam for boiling, some of the circumstances referred to ought to be kept in mind, such as the fact that steam cau-

not raise the temperature of the boiling liquid above 212°. Hence the conditions noticed of the raising the boiling point of water by the presence of matters held in solution, and by different kinds of vessels, do not apply to liquids when boiled by steam. This may be one cause of the observed difference of effect in the dye-house. Again, water boiled by passing a jet of ordinary pressure steam into it, never gets above 210°, a small deficiency, but sufficient to cause a difference in the results of many operations in the workshop.

This fact may be accounted for by the circumstance that in this process there is no attraction of the water by the surface of the vessel, as when boiled by fire, which, as has been observed by Berzelius, causes the boiling point in different vessels to vary upwards of 2°. In boiling by steam, no such attraction has to be overcome as that between the vessel and water; hence the boiling point is lower, and 210° may be actually the true boiling point of water. For all ordinary purposes, however, steam, as a heating agent, is of the highest value to the dyer.

Chemical Effects of Heat upon Colours.—The effects of heat in relation to chemical combination and decomposition, are of the utmost importance in all the operations of the dyer. The influence of heat in producing particular tints and colours, and also upon many colours when produced, are subjects of every-day observation. Nevertheless, the consequences are often so important, that the subject cannot be too fully impressed upon the minds of all interested. We shall, therefore, enumerate a few of the more prominent effects in this place.

In making a decoction of quercitron bark, for dyeing yellow, if it is made at a temperature of about 90°, a much finer and purer yellow is obtained than when the decoction is made by boiling. When woollen cloth is dyed by bark, and then hot-pressed, the heat impairs the colour; but generally dyed colours are more liable to be affected by heat when moisture is present, than in a dry atmosphere. For instance,—a safflower red will stand a high temperature when the air is dry, but if moisture be present, it passes rapidly into a yellowish brown. If a Prussian blue be placed in a moist atmosphere, and raised to the temperature of about 300° Fah., it fades entirely in a few hours. Many of the colouring matters of flowers, when imparted to cloth, may be dried without change in the cold and dark, and afterwards

be submitted to a temperature of 200° without alteration, but could not stand a temperature of 95° without being altered were these precautions not taken: such colours, therefore, if put on goods, could not be dried in a stove.

The kind of material on which the colour is dyed also influences the effects of heat. Indigo blue dyed upon cotton is permanent, exposed to heat and moisture; but the same colour, with the same dye-stuff, upon silk, is readily changed under those conditions. Safflower colours upon silk and cotton, placed under similar circumstances in regard to heat and moisture, are affected oppositely; that on the cotton is completely destroyed before that upon the silk is at all affected.

Thus we find that heat operates upon colours differently when the heated atmosphere or colour is dry and when it is moist, which suggests the propriety of paying strict attention to the condition of the drying-stove, and the hanging of the coloured fabrics, so as to give a free outlet to all moisture. If this is neglected, the colours are subjected to a hot vapour bath, and are under the most favourable conditions to be destroyed by the joint action of the heat and steam.

The same kind of colouring matter fixed upon cotton by different mordants, is affected by heat differently, whether moisture be present or not. This can be observed daily of logwood colours, when fixed by tin or by alumina. The different changes which these colours undergo in the process of drying, and the dependence of these upon the state of the stove, as to being *hot and dry*, or *hot and moist*, are familiar to the practical dyer. But as we shall have occasion to notice some of these changes when describing the dye-stuffs, and the colours produced, we pass over the details in this place. The following, however, may be stated as a general rule, namely—that all organic colouring matters are destroyed at a red heat. There are some, however, such as indigo, which sublime, or may be distilled by a heat less than sufficient to effect their destruction. Those colouring matters which are volatile, are in general most permanent when fixed upon fabrics, and resist the action of heat best; and those colours that do not sublime, are most susceptible of decomposition under the combined influence of air, heat, and moisture.

LIGHT.

Nature of Light.—The effects of light upon colours are so closely related to that of heat, and so powerful—particularly the direct rays of the sun—that we cannot pass over the consideration of those accidental phenomena, which we must understand as independent altogether of that essential relation which light has to produce colour. Strictly speaking, colours have no material existence, but are altogether the effect of light—at least colours do not exist in the objects appearing coloured, but in the light which is reflected from the apparently coloured object. In order, then, to define colour, we may briefly state what is known upon the nature and composition of light—at least so far as is necessary for our present purpose.

A beam of light is composed of three differently coloured rays—red, blue, and yellow—termed sometimes the *luminous*, *calorific*, and *chemical* rays, from their different properties of giving out heat and light, or in exciting chemical action. When a beam of light strikes the surface of a body, it bounds off as an elastic ball would do striking the same surface, and this bounding off is termed réflection; or, it is absorbed by the body and disappears, and is altogether extinguished; or, lastly, it passes through the body, making it transparent. In the first case, the bounding or reflected rays pass into the eye, and the body from which it is reflected appears white, or some particular colour. In the second place, there can no light proceed from the object to the eye, it being absorbed and extinguished—the body, therefore, is invisible; or, if the surrounding objects are illuminated, or reflect light, it appears black; and, in the third place, the light passing through unaltered, the body appears clear. The less the light is altered, the more clear and transparent the body, and consequently the more nearly invisible. Thus, that which we are accustomed to call white light is the simultaneous transmission of three coloured rays. Thus also, when light is admitted into

a dark room through a small aperture—say a hole in a window-shutter—and a glass prism is placed in the aperture, so that the light passes through it, and is made to fall upon a sheet of white paper, the light is decomposed, and appears upon the paper in the following order of colours :—

Violet.	Green.	Orange.
Indigo.	*Yellow	*Red.
*Blue.		

These are termed the seven prismatic colours, and the share they all occupy is termed the spectrum, of which each occupies a definite breadth. Those marked by a * are the only simple colours—that is, requiring no admixture—the others are produced by a mixture of different colours, and are therefore compound. The violet and indigo, for example, are composed of a mixture of blue and red: the green is a mixture of blue and yellow, and the orange of yellow and red. Hence, the primary colours are *blue*, *red*, and *yellow*. The equal admixture of these three colours gives white light; but any thing disturbing that simultaneous equality, produces a colour according to the nature and amount of disturbance. Thus, the prism through which the light entered the room, in the experiment referred to, from its shape and properties effects a complete disturbance, and the different colours are made visible. Similar effects are produced, as has been already stated, when the light is reflected from a surface. If the different coloured rays are not reflected or absorbed in the same ratio, the result is a colour according to the difference in the reflection or absorption of the different ray or rays. If the red ray is absorbed, and only the blue and yellow rays reflected, the object from which they are reflected appears green; if the yellow ray is also absorbed, the object appears blue; or if it has been the blue ray that is absorbed, and red and yellow reflected, the object appears orange; or if the yellow ray only is absorbed, the object appears violet or purple. Thus, by the rate of the disturbing influence, and the different combinations of these three colours, are all the various shades in nature produced.

Relation of Colours to the Fabric.—Although these remarks go to prove that colour has no material existence in the body appearing coloured, still the question is one of chemical science.

As every chemical change affects the character of the substance in its relations to light, the dyer's object is to effect a combination with his stuffs that will produce certain effects upon light, and thereby produce colours. It is found, sometimes, that the nature of the fabric affects the beauty and tint of a colour. A chemical compound alone may be obtained that vies with nature, both in the beauty and brilliancy of its colour; but, when that is obtained within the fibre of silk, cotton, or wool, the light must be transmitted through the material as a medium, and the fibre not being transparent, the original beauty of the colour is much diminished. Hence, the same colour, fixed within the fibres of those three substances, has different appearances in each; the cotton never yields the beauty of colour that the silk does, or even the wool. These circumstances, in all their relations, afford matter of constant study to the practical dyer.

It may be said that we cannot follow nature in the production of colours—that were the dyer to attempt to produce a white by an exact admixture of blue, red, and yellow, he would fail, and would produce instead a black, or deep brown; but this would not be a proper application of the law above stated. Nevertheless, to a certain extent, the practice of producing white by the combining the three colours, is had recourse to every day by the practical bleacher and dyer. All goods coming from the bleaching process, no matter what the nature of the process has been, have always a brownish yellow tinge: to cotton goods, a little indigo or cobalt blue is added, and the result is, a much purer white: to silk, which has much more of the yellow tinge than cotton, a little Prussian blue and cochineal pink, or what is more common, a little archil, which gives a violet colour, is added, the quantity varying according to the depth of yellow—the result is a beautiful white.

The following simple experiment serves to illustrate how far the production of colours depends upon the relation of the substance to light:—Take a solution of iodide of potassium, which is colourless and transparent, and divide it into three proportions: into the one pour a little acetate of lead, (sugar of lead,) into the other a persalt of mercury, and into the third a little starch, with a few drops of nitric acid. These are all colourless substances; but after they are mixed, in the first

we have a deep and beautiful yellow; in the second a red; and in the third a blue. Thus we have the three primitive colours produced by the same substance combining with other substances, all previously colourless. Many white flowers, when macerated in water, yield a yellow colour, which alkalies turn green and acids red.

Effects of Different Rays upon Colours.—The three separate rays of light have peculiarities of action: one has heating power, and is therefore termed the *calorific* ray; another has more of the property of giving light, and is termed the *luminous* ray; and the third has the greatest effect in changing the composition of bodies, and is in consequence termed the *chemical* ray. But, in our remarks upon the effects produced by light, we will speak of their total action.

The effects of heat upon dyed colours, which we have already described, are equally applicable to light, the presence of moisture greatly facilitating the effects. Reds, dyed by Brazil-wood and a tin mordant, exposed to light, pass into a brownish orange, and then gradually fade away. Prussian blue becomes reddish, and passes into a dirty grey. Yellows become brown, and then fade. The effects of light and moisture are beautifully shown by taking a piece of Prussian blue dry, and another wet, and placing each under a glass, exposed to the rays of the sun for a day. The wet piece becomes a reddish lavender, while the dry piece is very little affected. Safflower colours are easily affected by light, but more so when wet; so that when such colours are being dried in the air, care should be taken to keep them from exposure to light.

The action of light upon different matters and colours, and its power of changing the constitution of these substances, have recently formed the subject of a distinct branch of chemical study, known by the name of *actino chemistry*. Mr. Robert Hunt, who has done a good deal in this department of chemical science, says —"The changes produced by the influence of the solar rays are of a remarkable character, and few of them, in the present state of our knowledge, can be satisfactorily explained. In some instances it would appear that new properties are imparted to bodies by exposure to sunshine; in others that radiation has the power of disturbing the known chemical forces, and apparently establishing a new order of affinities; whilst, in all, we are forced to recognize the operations of a

principle, the nature of which is involved in the most perplexing uncertainty."

Effects of Light causing Combination.—We will here refer to a few examples of the action of light upon substances, and the power it possesses of inducing changes, with a view to impress upon the practical man the necessity of a strict attention to all the conditions and circumstances in which he may have to place his coloured fabrics and colouring materials. In many cases bodies remain mixed and without action upon each other in the dark, but combine rapidly and form new compounds when exposed to light. Thus, chlorine and hydrogen may be kept mixed in the dark for any length of time; but, if exposed to daylight, they silently combine and form muriatic acid. If the mixture be exposed to strong sunshine, the combination becomes so rapid as to cause an explosion.

Chlorine, in water, remains a long time unaltered in the dark, but by exposure to light the water is decomposed, muriatic acid is formed, and oxygen given off. These effects are observed daily in the operations of bleaching. If grey goods are put into the bleaching liquor, and kept in the dark, they whiten much more slowly than when exposed to light. Many bleachers know this, and expose their goods to light, and keep their bleaching vessels in the lightest part of the premises.

Mixtures of chlorine with carbonic oxide, of chlorine with sulphurous acid, and chlorine with pyroxilic spirit, and many other substances, are similar examples of the same kind, being all inactive upon each other in the dark, but combining easily and rapidly when exposed to light.

Light Decomposes Chemical Compounds.—Chemical compounds are also decomposed by exposure to light. Carbonic acid gas, exposed to strong sunshine, is decomposed into oxygen and carbon. This decomposition is supposed to go on daily in vegetable bodies during their growth, causing them to give off oxygen and take up carbon. Colourless nitric acid, exposed to the sun, soon becomes yellowish brown, from a portion of it being decomposed, and the red nitrous fumes remaining in the acid, produce the colour,—which again shows the propriety of keeping the carboys with that acid in the shade as much as possible, as such changes by the sun's

rays materially affect the preparation of many of the dyeing compounds, and also the strength of the acid.

Nitrate and chloride of silver—both white salts—become black by exposure to light: paper or cloth saturated with these salts, and exposed to light, is dyed permanently black. This is the principle of the new art, photography, which consists in exposing a piece of paper saturated with such salts, with a leaf or picture interposed between the light and the paper: an impression of the leaf or picture is thus obtained; and, by washing the paper afterwards in a solution of hyposulphite of soda, or weak ammonia, all the silver, not affected or decomposed by the light, is dissolved and removed, and the picture thus fixed. A piece of paper prepared with a solution of silver, and exposed to the coloured rays passing through a prism as described (page 11) is affected thus:—

Names of coloured ray.	Change on paper prepared.
Violet,	Purplish black.
Indigo,	Black not so purplish.
Blue,	Black.
Green,	Green.
Yellow,	Red.
Orange,	Faint brick red.
Red,	No change.

These results are exceedingly curious and interesting, and may point out some useful application in respect to the preserving of compounds from change, by keeping them in vessels which admit those rays only which least affect them.

Bichromate of potash put upon cotton fibre becomes dark brown by exposure to light.

Chromate of copper, a brown substance, passes into white by exposure to the sun's rays.

Solutions of substances are also affected by the sun's rays, sometimes sufficiently to cause a precipitation. A solution of proto-sulphate of iron (copperas) in distilled water, may be kept a long time clear in the dark; but, when exposed to sunshine, it becomes cloudy, and oxide of iron precipitates. A solution of bichromate of potash, exposed to the sun's rays, acquires a property of precipitating many metals, as chromates, much darker than will be produced by a similar solution kept in the dark. The reddening and darkening of *chrome* colours

by exposure to light is well known to dyers. The great effects of light upon precipitates are well known to the manufacturers of lakes—which, let it be borne in mind, are simply the colouring matter which constitutes the dyes, precipitated and dried—and, therefore, the effect produced upon these precipitates is equally true of the same colours as dyes. Sir H. Davy gives the following anecdote of a maker of carmine—a lake made from cochineal :—

"A manufacturer of carmine, who was aware of the superiority of the French colour, went to Lyons for the purpose of improving his process, and bargained with the most celebrated manufacturer in that city for the acquisition of his secret, for which he was to pay £1000. He was shown all the process, and saw a most beautiful colour produced, but he found not the least difference in the French mode of fabrication and that which had been constantly adopted by himself. He appealed to his instructor, and insisted that he must have kept something concealed. The man assured him he had not; and invited him to inspect the process a second time. He minutely examined the water and the materials, which were in every respect similar to his own; and then, very much surprised, said—'I have lost both my labour and my money, for the air of England does not admit us to make good carmine.' 'Stay,' said the Frenchman, 'don't deceive yourself; what kind of weather is it now?' 'A bright sunny day,' replied the Englishman. 'And such are the days,' said the Frenchman, 'on which I make my colour; were I to attempt to manufacture it on a dark and cloudy day, my results would be the same as yours. Let me advise you, my friend, only to make your carmine on bright sunny days.'"

Practical Application of the Principles.—In the application of some of these phenomena to the trade, we must pause and inquire experimentally how this can be effected. For instance, if we dissolve a piece of iron in nitric acid, and expose a portion of this solution for some time to the rays of the sun, and keep the other portion in the dark, on adding a solution of prussiate of potash to each of these, the precipitate formed by the portion exposed to light will be much deeper in colour than that kept in the dark. Were we to reason directly from the result, we would expose our nitrate of iron solutions to the light in order to have a deeper dye; but if we test this by ex-

periment, and dye a piece with each of the iron solutions, it will be found that the darkest blue is obtained from the iron solution kept in the dark. Thus, we observe, without experiment we may be liable to reason falsely. The change effected upon the iron by the light may make it less fit to enter within the pores or cells of the fibre; or if the combination of the stuff and fibre be affinity, these relations are affected—which we will discuss more fully in another part of this work.

These brief notices of the more prominent effects of light upon colours, and other compounds, will serve to impress the dyer with the importance of attending to what he too often considers trifling circumstances; and to show that while every different condition—the moisture of the air, the temperature, the degree of light, &c., are all acting and reacting upon the substances composing his colours, both before and after they are fixed upon the fabric, nothing should be considered too trifling or of too little consequence to warrant its being overlooked.

The consideration of the chemical changes which are supposed to be taking place in the vegetable kingdom through the influence of light, will be more fully explained when we are treating of the colouring matters of vegetables.

In connection with light, there is an application of a very important practical kind which it will be well to notice, namely, the arrangement of colours, so that their harmony should produce the best effect. Upon this subject many propositions were made for the decoration and laying out the manufactures in the Great Exhibition. Upon the philosophy of the arrangement of different colours for effect, we will quote, from the *Athenæum*, (*Athen.* 1851, *page* 273), a few passages upon this subject, which we think will be useful to the dyer:—

"The 'successive' contrast has long been known; and it consists in the fact, that if you look steadfastly for a few minutes on a red surface fixed on a white sheet of paper, and then carry your eye to another white sheet, you will perceive on it not a red but a green one; if a green, red; if purple, yellow; if blue, orange. The 'simultaneous' contrast is the most interesting and useful to be acquainted with. When two coloured surfaces are in juxtaposition, they mutually influence each other—favourably, if harmonizing colours, or in a contrary manner if discordant; and in such proportion in either case

as to be in exact ratio with the quantity of complementary colour which is generated in our eye. For example, if two half-sheets of plain tint-paper—one dark green, the other red—are placed side by side on a grey piece of cloth, the colours will mutually improve, in consequence of the green generated by the red surface adding itself to the green of the juxtaposed surface—thus increasing its intensity—the green in its turn augmenting the beauty of the red. This effect can easily be appreciated if two other pieces of paper of the same colours are placed at a short distance from their corresponding influenced ones, as below:—

RED. RED GREEN. GREEN.

It is not sufficient to place complementary colours side by side to produce harmony of colour, the respective intensities having a most decided influence: thus pink and light green agree—red and dark green also; but light green and dark red, pink and dark green do not; therefore, to obtain the maximum of effect and perfect harmony, the following colours must be placed side by side, taking into account their exact intensity of shade and tint:—

HARMONIZING COLOURS.

Primitive Colours.	Secondary Colours.	
Red	Green	Light blue.
		Yellow.
		Red.
Blue	Orange	Red.
		Yellow.
		Blue.
Yellow orange	Indigo	Blue.
		Red.
		Yellow.
Greenish yellow	Violet	Red.
		Blue.
		Yellow.
Black	White	Yellow.
		Blue.
		Red.

"If respect is not paid to the arrangement of colours according to the above diagram, instead of colours mutually

improving each other, they will, on the contrary, lose in beauty: thus, if blue and purple are placed side by side, the blue throwing its complementary colour, orange, upon the purple, will give it a faded appearance; and the blue receiving the orange-yellow of the purple, will assume a greenish tinge. The same may be said of yellow and red, if placed in juxtaposition. The red, by throwing its complementary colour, green, on the yellow, communicates to it a greenish tinge; the yellow, by throwing its purple hue, imparts to the red a disagreeable purple appearance. It is of very great importance that every one should be acquainted with the laws of colours who intends to display or arrange coloured goods or fabrics.

"The mixed contrast gives the reason why a brilliant colour should never be looked at for any length of time if its true tint or brilliancy is to be appreciated; for if a person looks, for example, at a piece of red cloth for a few minutes, green, its complementary colour, is generated in the eye, and adding itself to a portion of the red, produces black, which tarnishes the beauty of the red. This contrast explains why the shade of a colour may be modified according to the colour which the eye has previously looked at, either favourably or otherwise. An example of the first instance is noticed when the eye first looks to a yellow substance and then to a purple one; and as exemplifying the second case, looking at a blue and then at a purple."

ELEMENTS OF MATTER.

Differences between an Element and Compound.—It has been intimated that the conditions of matter—solidity, fluidity, and gasuity—depend upon heat; and it was also stated that, in each state, there is a vast variety—a variety so great that the idea of telling where their conditions begin and end is a task seemingly beyond human power. Nevertheless, by labour, by experiment, and comparison, much has been done not only to distinguish every variety of substance, but why one substance differs from another both in appearance and quality. Let us take a known compound as an illustration: When a piece of steel is placed into diluted sulphuric acid, the acid dissolves the greater part of it; but there is left undissolved a black matter, which, by testing, we find to be charcoal or carbon, and that which has been dissolved is iron. We therefore infer that steel is composed of iron and charcoal—that it is a *compound* substance; but if we take the carbon, and treat it in any way within our power, we find it still the same, *without* components. In the same manner let us test iron—dissolve it, melt it, or treat it as we will, it yields nothing but iron. All such substances, then, that resist every effort to decompose, or show any admixture, are termed elementary, or simple substances. The number of such elements known to the chemist at the present time are sixty-two, and all the varieties in which we find matter presenting itself to us—whether in the mineral, the vegetable, or the animal kingdoms—are made up of one, or a mixture of two or more of those sixty-two elements. The following table gives the names and particulars necessary to be observed in the study of these elements:—

Aluminum	Al	= 13·7	
Antimony	Sb	=129	
Arsenic	As	= 75	
Barium	Ba	= 68·5	
Beryllium	Be	= 4·7	
Bismuth	Bi	=213	
Boron	B	= 10·9	
Bromine	Br	= 80	
Cadmium	Cd	= 56	
Calcium	Ca	= 20	
Carbon	C	= 6	
Cerium	Ce	= 47	
Chlorine	Cl	= 35·5	
Chromium	Cr	= 26·7	
Cobalt	Co	= 29·5	
Copper	Cu	= 31·7	
Didymium	D		
Erbium	E		
Fluorine	Fl	= 18·9	
Gold	Au	=197	
Hydrogen	H	= 1	
Iodine	I	=127.1	
Iridium	Ir	= 99	
Iron	Fe	= 26	
Lanthanium	La	=	
Lead	Ph	=103·7	
Lithium	Li	= 6·5	
Magnesium	Mg	= 12.2	
Manganese	Mn	= 27·6	
Mercury	Hg	=100	
Molybdenum	Mo	= 46	
Nickel	Ni	= 29·6	
Niobium	Nb		
Nitrogen	N	= 14	
Norium	No		
Osmium	Os	= 99·6	
Oxygen	O	= 8	
Palladium	Pd	= 53·3	
Pelopium	Pe		
Phosphorus	P	= 32	
Platinum	Pt	= 98·7	
Potassium	K	= 39·2	
Rhodium	R	= 52·2	
Ruthenium	Ru	= 52·2	
Selenium	Se	= 39·5	
Silicium	Si	= 21·3	
Silver	Ag	=108·1	
Sodium	Na	= 23	
Strontium	Sr	= 43·8	
Sulphur	S	= 16	
Tantalum	Ta	=184	
Tellurium	Te	= 64·2	
Terbium	Tb		
Thorium	Th	= 59·6	
Tin	Sn	= 59	
Titanium	Ti	= 25	
Tungsten	W	= 95	
Uranium	U	= 60	
Vanadium	V	= 68·6	
Yttrium	Y		
Zinc	Zn	= 32·6	
Zirconium	Zr	= 22·4	

When two or more of these elements combine together, it is found that the union does not take place indeterminately, but always in definite proportions. Those proportions are expressed by the figures placed opposite to the names in the above table. For example, if we mix together one ounce of hydrogen and one ounce of oxygen, and bring them under circumstances to cause combination, it is found that the one ounce of oxygen has combined with an eighth part of the hydrogen, or two drams, and that other seven ounces of

oxygen are required to combine with the whole of the hydrogen. Their combining properties are therefore set down as 1 to 8. The same law holds good for every other element; so that the union is invariably distinct and definite. One element, however, is often found to combine with another in a greater number of proportions than one to one. Thus, suppose nitrogen—which, according to the table, has a combining weight of 14—combines with oxygen in proportions as under:—

One nitrogen = 14 to one oxygen = 8.
One nitrogen = 14 to two oxygen = 16 two times 8.
One nitrogen = 14 to three oxygen = 24 three times 8.
One nitrogen = 14 to four oxygen = 32 four times 8.
One nitrogen = 14 to five oxygen = 40 five times 8.

Thus we observe that the proportion of oxygen is always 8, or a multiple of 8; so it is with nitrogen, always 14, or twice 14, and so on to any number of multiples of 14. The same rule holds good with every element in the table; they combine only according to the number following the name.

But when they thus combine in different and distinct quantities, the compounds formed are also distinct and definite. Thus, one portion of nitrogen and one oxygen is laughing gas; and it is so at all times and under all circumstances, and can be nothing else. But when two of oxygen combine to one of nitrogen, a different substance is formed from laughing gas, also distinct and definite from every other proportion in which the elements unite. The first and last of the above list is an apt illustration—the former being laughing gas, the latter *aquafortis*—nitric acid.

Use of Symbols.—The letters placed immediately after the names of the elements in the above table, are the symbols commonly used to represent the respective elements, and facilitate the expression of the compounds into which they enter. Thus, to represent laughing gas, we write N O, which means one of nitrogen and one of oxygen. The symbol always represents the weight of the *proportion*, as given in the table; and the figures attached show how often that proportion is repeated. Thus, the formula for aquafortis, NO_5, which means one part of nitrogen and five of oxygen—the figure

being placed immediately after the symbol which is multiplied. Were there two of nitrogen and one oxygen, the formula would be N_2O; but sometimes there may be two or more proportions of a compound combined with another compound: this is represented by placing the figure before the compound to be multiplied, and a comma at the end. For example,—two proportions of aquafortis united with one of water is expressed thus, $2NO_5$, HO. The figure 2 applies to all between it and the comma. Some use the sign + instead of a comma —thus, $2NO_5$,+HO. It being important to the student that these be fully understood before beginning to read for study, we will take another series of compounds :—

SO_3 one sulphur, three oxygen, sulphuric acid.
SO_3+HO sulphuric acid with one water.
$2SO_3$+HO two sulphuric acid with one water.
SO_3+2HO sulphuric acid and two water.
SO_3+3HO sulphuric acid and three water.
SO_3+FeO or SO_3, FeO sulphuric acid and oxide of iron.
SO_3FeO+HO sulphuric acid, oxide iron, and water.
SO_3FeO+5HO sulphuric acid, oxide of iron, and five water.
$3SO_3$, Fe_2O_3+9HO, here we have three of sulphuric acid, two of iron, three of oxygen, and nine water, which is the formula of one of the salts of iron.

To make up the equivalent weight of any compound from symbols, we have simply to multiply the elements given according to the table. Thus, suppose we take the sulphuric acid and two water, which is strong vitriol, we have

One sulphur,.....equivalent weight, 16	=	16
Three oxygen,.....8×3	=	24
Two water,.....1 Hy. and 8 oxygn...=9×2	=	18
		58

which is the proportion or weight of sulphuric acid of the strength which would be required to combine with any other element, suppose iron, which is 28; therefore it would require fully twice the weight of sulphuric acid of this strength to that of a piece of iron to dissolve it.

The following formula of crystallized alum will serve as an exercise for the student upon the symbols and equivalents:—

. $KOSO_3$, Al_2O_3 $3SO_3+24HO$.

Some chemists, instead of using O for oxygen, express it by a simple . —thus sulphuric acid will be $\dddot{S}$, or the alum—

$\dddot{K}\dddot{S}$ $\dddot{A}l_2$ $3\dddot{S}$ $24\dot{H}$.

Nomenclature.—In the nomenclature of these elements in the above table there has been no definite rule, being named either from the fancy of the discoverer, or from some leading property or appearance they present, which will be noticed under their separate descriptions; but, in naming compounds, a distinct rule has been adopted, so that the name of the compound expresses, as nearly as possible, its composition and property. We will give a few of the leading principles observed in this rule of naming compounds.

Rules for Naming Compounds.—When two *elements* combine together, and the compound formed has not acid properties, the name ends in *ide*, such as *oxide*, *chloride*, *bromide*, *iodide*, &c. Sometimes *uret* is used instead of *ide*, such as in *sulphuret*, *carburet*, *phosphuret*, &c.; but *ide* is now most generally adopted even for these, giving *sulphides*, *carbonides*, *phosphides*, &c. When the compound formed by the union of the elements has acid properties, the name ends in *ic*, or *ous;* thus we have *sulphuric*, *sulphurous*, *nitric*, *nitrous*, *chloric*, and *chlorous* acids; but these elements, uniting together in different multiples, have prefixes added to express the number of proportions. Thus, *proto* denotes one proportion, or first; *deuto*, or *bi*, two proportions; *trito*, three proportions; *per* denotes no particular number only the highest proportion. As examples, take the compounds of hydrogen and nitrogen, already noticed:—

NO protoxide of nitrogen.
NO_2 binoxide of nitrogen.
NO_3 nitrous acid.
NO_4 peroxide of nitrogen.
NO_5 nitric acid.

Thus, we observe, the full name of the substance not having

acid properties denotes its composition. In the case of acids, it does not tell the number of elements combined, as with oxides—*ous* simply signifying that it has less oxygen than another acid composed of the same elements, and which ends in *ic*. There are sometimes more than two acids formed by the combining of the same elements; in this case, if the oxygen is less than in the acid whose name terminates with *ous*, the prefix *hypo* is put to the name of the *ous acid;* if there be more oxygen than in the *ous* acid, and less than the *ic* acid, the same prefix is made to the last-named acid. Finally, when there is more oxygen present than in the acid whose name terminates with *ic*, the prefix *per* is put as in oxides. The following illustrations will exemplify these terms:—

S_2O_2 hypo-sulphurous acid.
SO_2 sulphurous acid.
S_2O_5 hypo-sulphuric acid.
SO_3 sulphuric acid.

Any acid found having more oxygen, in relation to the sulphur, than the last named in this list, would be called *per*-sulphuric acid. It will thus be seen that the names of the compounds denote their composition, and give an idea of their leading properties. The term *sesqui*—as *sesquioxide*—is often used, and means one and half of an equivalent, which, as may be inferred from what has been said, cannot take place. Nevertheless, the name is conveniently retained to denote such compounds as have two of one element and three of another—such as sesquioxide of iron, also termed peroxide, and which is composed of two iron with three oxygen, Fe_2O_3. Sometimes one proportion of oxygen, chlorine, &c., combines with two proportions of a base as a metal; such compounds have the prefix *sub*, or *di*, as

Fe_2O, sub-oxide of iron, or dinoxide of iron.
Cu_2Cl, sub-chloride, or dichloride of copper.

When one proportion of oxygen, chlorine, &c., combines with three of a metal, the prefix *trisub* or *tridi*, is occasionally used, but this is not very convenient; the best and most general plan is to denote such compounds as *basic*, and then apply the ordinary prefixes, such as bibasic, tribasic, &c., thus:—

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Cu_2O, bibasic oxide of copper.
Cu_3O, tribasic oxide of copper.

In the name of a compound ending in *ide*, the base or element with which the oxygen, chlorine, &c., is combined, is named last, as

Oxide of iron.	Oxygen and iron.
Chloride of iron.	Chlorine and iron.
Iodide of iron.	Iodine and iron.
Oxide of sulphur.	Oxygen and sulphur.
Oxide of nitrogen.	Oxygen and nitrogen.

But with compounds having acid properties, the base is placed at the beginning, thus:—

Sulphuric acid.	Sulphur and oxygen.
Nitric acid.	Nitrogen and oxygen.
Hydrochloric acid.	Hydrogen and chlorine.

Salts--Their Nature and Nomenclature.—The acids combine with other substances, as the metals, and form another class of compounds termed Salts. The names of these also denote their composition: the salt formed between the acid terminating in *ic* and a base, ends with *ate;* that formed by the acid terminating in *ous* ends with *ite*, the name of the element with which the acid combines being added. Thus,

Sulphuric acid and iron form *sulphate of iron.*
Sulphurous acid and iron ..... *sulphite of iron.*

When these acids unite with elements or bases in different proportions, the same prefixes are used as with oxides. If one proportion of acid unites with one of another element, the compound is termed *proto*—as proto-sulphate of iron; if two of acid and one metal, the compound has *bi*—as bisulphate of iron, &c. *Per* is also used as denoting the highest proportion, as when three equivalents of acid unite with two equivalents of iron, the salt is termed *persulphate of iron.*

Sometimes we have the metal uniting with acids, forming basic salts, as described in the case of the basic oxides, such as having two proportions of metal to one of acid, and three proportions or equivalents of metal to one of acid. In such cases, the same prefixes are used as we have before stated, namely,—

bibasic sulphate of copper, two equivalents of copper to one of sulphuric acid; *tribasic* sulphate of copper, three copper to one acid.

Combinations of water with oxides or salts are termed *hydrates*, or the compound is termed *hydrous*, in contradistinction to substances having no water, which are termed *anhydrous*—thus, hydrate of potash, or hydrous potash, KO HO; anhydrous potash, KO.

Two salts sometimes unite together, and form a definite compound, which is termed a double salt. Alum, as already given, is a good instance of this class of compounds: it is a double salt of sulphate of alumina and sulphate of potash.

CHEMICAL AFFINITY.

The elements of matter have a disposition, if we may use the term, to unite with one another: this disposition is termed *affinity*, or chemical attraction. The affinity of any one element for the others is not equal, but is greater for some one element, or, for a particular class of elements. Thus oxygen has a stronger attraction for those elements, the combining with which forms alkalies, than for any of the others; and amongst these potassium has the strongest affinity for oxygen, so that, by the operation of this law, should a number of elements be arranged together, under proper circumstances for combining, those which have the strongest attraction for each other will combine first. The same law holds good when compound bodies unite together, such as an acid with the oxide of a metal. Were we to take sulphuric acid, and add to it a mixture of potash and magnesia, the acid would combine with the potash before it would take the magnesia; and were there enough of potash to combine with the whole of the sulphuric acid, the magnesia would be left, because the potash has a stronger attraction for this acid than magnesia. This peculiarity of selecting is not merely owing to the substance having acid properties, but from a peculiar attraction between the base and acid compounds. Thus the two acids, *sulphuric* and *muriatic*, comport themselves towards the following bases, as under:—

Muriatic Acid.	Sulphuric Acid.
Silver.	Barytes.
Potash.	Strontia.
Soda.	Potash.
Barytes.	Soda.
Strontia.	Lime.
Lime.	Magnesia
Magnesia.	Silver.

Although we have named silver here, under the sulphuric acid column, in order to complete the comparison, it is not immediately next to magnesia in affinity for that acid; a great many of the other metals rank before it, such as mercury, copper, iron, zinc. So that, were there a solution of sulphate of silver added to a solution containing these, the acid would leave the silver and combine with the mercury, next leave the mercury and combine with copper, then leave the copper and take the iron, and lastly leave the iron and take the zinc.

It is this law of affinity that regulates compositions and decompositions, all of which are matters of daily experience in the dye-house, particularly that class of decompositions termed double, in which two salts being put together, there takes place a mutual exchange of partners, if we may so term it. For instance, in mixing nitrate of iron with yellow prussiate of potash: the nitric acid leaves the iron, and combines with the potash, while the iron and prussic acid combine, forming Prussian blue. When any of the two compounds so combined forms an insoluble substance, the decomposition is always more apparent, more complete, and most applicable to dyeing purposes. Compounds which cannot easily be formed, directly by bringing their elements together, are often formed by means of double decomposition: thus carbonate of iron is difficult to form directly, but by mixing a solution of carbonate of soda with sulphate of iron, this compound is instantly formed, which may be thus represented—

$$NaO\ CO_2,\ FeO\ SO_3 = FeO\ CO_2,\ NaO\ SO_3,$$

Application of Affinity.—These double decompositions and recompositions are of the utmost importance to the practical dyer, who should make himself thoroughly acquainted with all their laws and conditions; as it is, these formations of new and often insoluble compounds, which constitute a prominent feature in the production of colours, and every circumstance connected with this class of phenomena, favour this kind of reaction for practical purposes. It is a general law in ordinary affinity, in the union of two elements, or of a compound with an element, such as dissolving a metal in acid, that there is always a great evolution of heat. This circumstance would interfere with many dyeing operations, both upon the fibre and colour; but in the double affinity referred to,

where two compounds merely exchange elements, there is no quantity of heat evolved, to interfere with the dyeing operations or fabric. The interchange of elements takes place quietly, so that the dyer may fix within the fibres of the most delicate material any compound required for the colour.

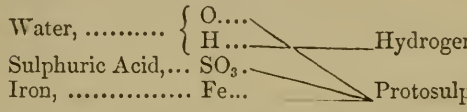
Circumstances influencing Affinity.—The force of affinity is greatly influenced by the conditions in which the combining bodies are placed, as indicated when treating of light and heat. Where the atoms of any body are brought into contact with another body, under more or less favourable circumstances, anything that diminishes the cohesion of the particles, allows those of the other body to come into closer approximation, and therefore favours chemical union. Solid bodies, in general, are without chemical action upon one another, therefore, before any chemical change can take place, it is necessary to bring the substance into a fluid state. This is eminently necessary in all dyeing operations, not only for the purpose of causing combination, but to enable the particles to enter within the fibres of the cloth, and to be, while there, acted upon by the affinity of another body, also in solution, brought into contact with them. This is an essential condition of all dye drugs, and of all salts used in dyeing, either as dyes or mordants, and must never be lost sight of in studying either its philosophy or practical operation, as anything that interferes with the free operation of these conditions or solubility, necessarily retards the process or deteriorates the dye.

Catalytic Influence.—Another circumstance or power sometimes occurring in dyeing operations, which interferes with or directs chemical affinity amongst the particles of bodies, is, that one body often induces a chemical change in another, while it undergoes no change itself. This kind of affinity, or power, is termed CATALYSIS. A good instance of this is in fermentation: a little yeast put into beer induces fermentation in all the solution, while the yeast is not altered. If we boil starch with dilute sulphuric acid, the starch is first changed into gum, and then into sugar. Yet notwithstanding these changes, the sulphuric acid is found unaltered, either in property or quantity. A great many substances possess this property of catalytic influence; and it is not unlikely that fibrous materials, such as silk, woollen, and cotton, possess it towards many of the vegetable colouring matters used in dyeing; indeed many oper-

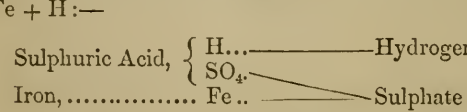
ations in the dye-house indicate the presence of some such power. The real nature of this power is not well understood; only we know that bodies subject to change by catalysis have their particles held together by a weak affinity, and therefore changes are less or more easily effected, according to the power exerted, to keep their elements together. The elements of many organic compounds seem held together by a balance of power among them, so that while another substance put into such a compound may possess a sufficient attraction for some of the elements in the compound, to disturb this balance of power, yet it may not have sufficient power to combine with them, but only cause the whole elements to re-arrange themselves in a new, and probably more stable, form. The study of such reactions is of the greatest interest; and as these principles of action, in all probability, play a prominent part in the art of dyeing, it will be again brought under consideration, when describing operations where we think this action takes place. We may here mention, however, that the introduction of such a term as *catalysis* is only considered useful as bringing under one group a certain class of phenomena; but indeed the same may be said of the no less useful term, affinity. When our knowledge of these hidden powers is more extended, all those phenomena may, perhaps, be accounted for, and ranged under the operation of some one universal power or law, of which at present we know only by particular terms.

Constitution of Salts.—It may have been observed that, in describing the constitution of compounds and their nomenclature, we grouped the elements together, as compounds, in a certain order, such as sulphate of protoxide of iron, FeO SO_3. This formula, by its term and grouping, it may be farther observed, indicates that the sulphuric acid is combined with the oxide of the iron, and not directly with the iron itself. Now there is a difficulty which attaches to the nomenclature, that the formula is made to indicate a certain definite arrangement of particles, which is now pretty generally considered as incorrect. However, it is not intended to enter here into the merits of the different views entertained by chemists regarding this point, but briefly to give a general idea as a guide to the workman. We will take sulphuric acid as our first illustration. The composition of this acid is given as SO_3, but SO_3 is a solid crystalline

compound, which has no acid properties until it is combined with one proportion of water, being then $SO_3^{\bullet} + HO$, or hydrous sulphuric acid. If into this acid we place a piece of iron, the reaction may be expressed thus, $SO_3HO + Fe = SO_3FeO + H$; or as follows:—



Here we have water decomposed, to give an atom of oxygen to the iron, forming an oxide; and then we have the acid combining with this oxide. The same principle of action is ascribed to all metals, and used to be described as a sort of disposing affinity. The acid SO_3 is conceived to have such an attraction for the oxide of the metal, that it disposes both the metal to combine with oxygen and the oxygen with the metal, in order that it might unite with the two, to form a salt. Sir H. Davy, with his usual clear perception of all chemical phenomena, thought, that as sulphuric acid SO_3 had no acid properties, and was incapable of combining with any body as such, except in union with water, it was more probable that what is termed hydrated sulphuric acid $SO_3 + HO$, may be the true composition of sulphuric acid, rather than SO_3, and ought to be represented thus, $SO_4 + H$. The hydrogen being the base or metal, and that its presence is an essential qualification to the acid, so that a piece of iron, being put into sulphuric acid, will have a reaction as under, $SO_4H + Fe = SO_4Fe + H$:—



Here we have no supposed primary-disposing action, but the iron simply taking the place of hydrogen, by substitution, in virtue of SO_4, having a stronger affinity for it than for the hydrogen. The same reaction explains the dissolving of any other metal in sulphuric acid. Names have been proposed in accordance with this theory, as, for instance, the SO_4 is termed *sulphion;* therefore, $SO_4 + H$, instead of being termed sulphuric acid, will be *sulphionide* of hydrogen, and sulphate of

iron, *sulphionide* of iron. Such names will, however, be very difficult to be introduced into the science; and although they were approved of, their use must necessarily be a matter of gradual growth. As the truths of these views become apparent, a new and improved nomenclature may grow up spontaneously.

The views given above, of the true formula of sulphuric acid, may be applied to all hydrated acids. Nitric acid of the formula NO_5 has never been isolated; its existence is merely supposed from analogy. There is $NO_5 + HO$, hydrated nitric acid; but why $NO_5 + HO$, rather than $NO_6 + H$? Any metals dissolving in it only replace the hydrogen. The same with muriatic acid which is a compound of hydrogen and chlorine, properly termed hydrochloric acid. In dissolving a metal in this acid, the acid, not the water, is decomposed. Or if we put hydrochloric acid upon the oxide of a metal, as soda, the action is not that of the acid combining with the oxide, but there is a double decomposition and composition, represented by $HCl\ HO + NaO = NaCl + 2\,HO$. So that bodies termed muriates are more properly chlorides.

Salt Radicals.—There is another thing necessary for the student to bear in mind, in reference to these views, and the nomenclature resting upon them. The SO_4, NO_6, &c., are called the *Salt Radical*, which term is often used in chemical books, and is applied equally to a compound, such as the above, or to an element, such as chlorine. It refers to any element, or compound, that will form an acid when combined with hydrogen, and a salt when united with a metal. There are a great many salt radicals which are compound substances, but which deport themselves in their reactions as elements. One eminent example of a substance of this kind is cyanogen, (C_2N) which is the salt radical of Prussic acid, and which we will have occasion to notice when treating of the compounds of this acid and the ferro-prussiates, so much used in the dye-house.

This view of the constitution of salts is much more simple than that of oxides combining with the acids, and, as it will be apparent, reduces the compound bodies, termed acids and salts, into one great class.

It also enables us to account for a remarkable law which has been already noticed, namely, that bases, such as metals, always unite with the same number of proportions, or equiva-

lents of acids or salt radicals. Thus, if we dissolve protoxide of iron in sulphuric acid, one proportion of iron only combines with one proportion of acid, and is represented by $FeO, SO_4H = Fe\,SO_4, HO$.

But if we take the peroxide of iron, and dissolve it in sulphuric acid, we then have three proportions of acid, thus—

$$Fe_2\,O_3,\ 3\,SO_4\,H = Fe_2\ 3\,SO_4HO.$$

It must, however, be borne in mind, that both theories require several hypothetical conditions to be taken for granted, to enable us to account for all the phenomena which take place in the actions of one body upon another; and also, that both these views of the constitution of salts, as to the manner in which the atoms or particles arrange themselves, are liable to objections. We have stated the fundamental principles of these views, both as a general guide to the student in his inquiries into chemical science, and because we will have occasion to refer to them hereafter. But the reader who wishes to obtain more extended information, may consult such works as those of Graham, Liebig, Daniell, Gmelin, and others, who have given this matter much close attention; and such research will be found amply to repay any labour and time expended upon it, for on the proper understanding of the fundamental laws of affinity depends, in a great measure, the proper application of chemical science to practical purposes, and more especially in such delicate operations, and with such materials, as the animal and vegetable fibres operated upon in a dye-house.

ELEMENTARY SUBSTANCES.

Oxygen (O. 8.)

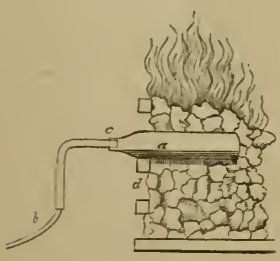
By referring to the table of elements, it will be found that several substances are therein named which many of our practical readers have never heard of. There are, indeed, a number of elements of which little more is known than the fact of their existing in certain compounds; they have only been seen by the discoverers and a few friends, and are as yet so rare, and found in such small quantities, that, under present circumstances, their application to any common branch of manufacture is not thought of. Such substances we will therefore pass over with a very short notice, and confine ourselves more to those that are, or, so far as their cost and quantities are concerned, may be brought into common use. The name of the element at the head of this chapter is a very familiar term in the dye-house, but is applied so indiscriminately, and so often erroneously, to different substances, as to cause a considerable misunderstanding of its real nature and properties. Many of these erroneous applications of the name, and consequent confusion of ideas, will be noticed more appropriately under chlorine, with which gas, oxygen is often identified in the dye-house.

Oxygen exists in Nature both free and combined: when free, it forms a colourless and transparent gas, without taste or smell; it is a little heavier than common air, of which it forms a part, and is dissolved or absorbed by water, in the proportion of from 3 to 4 per cent. by weight. Its wide range of affinity for other elements, its presence in almost every compound, and the part it plays in nature, invest it with an importance not possessed by any of the other elements. It constitutes more than a fifth part of the atmosphere, as much as eight-ninths of the water, and fully half of the solid crust of the globe; and it is, besides, a prominent ingredient in all

animal and vegetable bodies. The following table shows its numerical importance more precisely:—

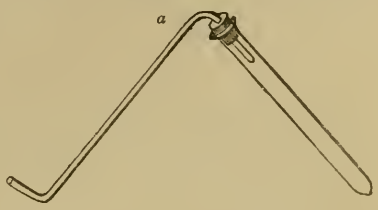
Water has	8	oxygen in	9	by weight.
The Air,	3	„ in	9	„
Crust of the Earth,	5	„ in	9	„
Animals and Vegetables,	7	„ in	9	„

How to Make Oxygen Gas.—The name oxygen was given to this element from the idea which the old chemists had, that it gave acid properties to its compounds. It was first recognized in this country as a distinct substance by Dr. Priestley, in the year 1774, and about a year after in Sweden, by Scheele, without any previous knowledge of Priestley's discovery. It was obtained by Priestley by heating, in a retort, red oxide of mercury, which is thereby resolved into fluid mercury and oxygen. But other and more economical means are now adopted for its preparation, as follows:—An iron bottle is prepared, with an iron tube fitted into the mouth air tight, forming a retort; into this a quantity of black oxide of manganese is put, and the bottle placed with its contents, into a good fire, with the open end of the iron pipe dipping into a vessel filled with water. The following figure shows the bottle in the fire, with the conducting pipe. Care must be taken not to allow any of the contents of the bottle to get into the pipe. When the bottle becomes red hot, bubbles of gas are seen to rise from the pipe through the water: these bubbles are oxygen gas, and may be collected by filling a bottle or jar with water, and holding its mouth downwards over the extremity of the pipe; the gas, ascending into the bottle or jar, gradually displaces the water. In explanation of what is taking place within the retort-bottle in the fire, it may be stated, that black oxide of manganese is composed of $Mn\,O_2$; the high heat drives off, or sets at liberty, a portion of the oxygen, and the manganese is converted



into a lower state of oxidation, so that 3 Mn O_2 becomes Mn_2 O_3, Mn O + 2 O.

Another and more rapid method of preparing oxygen is, by taking equal parts of oxide of copper and chlorate of potash, and placing the mixture into a small flask or test tube, fitted with a glass tube, as represented by the annexed cut. When heat is applied, by means of a lamp, a rapid evolution of gas takes place, very pure, and without any danger to the operator. One ounce of chlorate of potash, treated in this way, will yield about 500 cubic inches of gas. The chlorate of potash is composed of KO Cl O_5, all the oxygen is set free, and chloride of potassium left. The oxide of copper undergoes no decomposition. The part it plays is not well understood; but a practical use of its presence in this experiment is, to prevent fusion of the salt, which would take place, and is liable to break the vessel used. When the experiment is finished, and the flask cold, a little water will dissolve out the chloride of potassium from the oxide of copper, which, when dried, may be used again for a similar experiment. There are a variety of other means of obtaining this gas, but they need not be detailed.

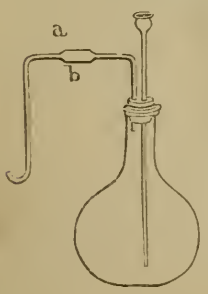


Properties of Oxygen.—Oxygen is an eminent supporter of combustion. If a candle be placed in an atmosphere of this gas, it burns with intense brilliancy. Sulphur and charcoal being kindled, and placed in oxygen, give a vivid light, and there is formed sulphurous acid with the sulphur, and carbonic acid with the charcoal. If a piece of iron or steel wire be made red hot, and then immersed into oxygen gas, the combination is so rapid, that the heat produced causes the iron to scintillate, and the oxide to fuse, and drop off like water, sufficiently hot to melt or fuse china and glass. Many other metals burn in the same way as iron in this gas. It is upon this gas depend the processes of combustion and respiration; and the various functions of organized existence, in all its forms, are essentially connected and sustained

through the agency of oxygen. Indeed there are few operations in chemistry which are not in some way connected with oxygen, so that, under the various heads in which we intend to treat our subject, its nature and properties will be constantly developed. Dyed fabrics, whether wet or dry, suspended in this gas, are not affected, a fact for the dyer to bear in mind when he is identifying this gas with chlorine.

Hydrogen (H. 1.)

Hydrogen is a gaseous element, never found free or uncombined in Nature, but is easily obtained from some of the compounds of which it is a component. When pure, it is without smell or colour, and is the lightest substance known; it is therefore used for inflating balloons. Its distinctive character as an element was first pointed out by Cavendish, in 1766. It exists abundantly in nature, in combination with other elements; it is a constituent of all animal and vegetable substances; and, being one of the constituents of water, it enters as such into the composition of almost all compounds.



It is from the decomposition of water that hydrogen is generally prepared for experimental purposes. The process is simple. By putting some iron or zinc into a retort, and pouring over it a little dilute sulphuric or hydrochloric acid, the metal dissolves with effervescence, and the gas, in passing off, may be caught in bottles or jars over the pneumatic trough, as described for oxygen. Instead of a retort, a flask, or bottle, may be used, having a tube fitted by a cork in the mouth of the bottle, as represented by the annexed figure.

The reaction which takes place, by the acid acting on the metal, is as we have before shown, (page 32,)

$$SO_4H + Zn = SO_4Zn + H.$$

We observe here that the change is only the substitution of the metal for the hydrogen in the acid. The use of the

water mixed with the acid is to dissolve the salt of zinc formed in the process, which requires a considerable quantity of water. From these and similar facts, hydrogen is supposed to be a metal existing in a gaseous form. At all events, its chemical character exhibits many of the properties possessed by the metals. Hydrogen, when prepared in the way described, has a slight smell, which results from impurities in the substances used, generally a small trace of arsenic, or sulphur, in the metal. When iron is used instead of zinc, the smell is still more perceptible. Hydrogen is a combustible gas, and burns with a yellow flame, but does not support combustion. A burning candle immersed in it is instantly extinguished. When mixed with oxygen, and heat is applied, the mixture explodes with a loud report, and water is formed by the union of the gases. Hydrogen does not support life. An animal immersed in an atmosphere of it soon dies. Several attempts have been made to breathe this gas, and some curious effects have been observed, but from incautiousness in not purifying the gas perfectly before inhaling it, two fatal accidents have followed. All such attempts are extremely foolish. Hydrogen combines with oxygen in two proportions, forming the protoxide or water, and peroxide or binoxide, a substance which has strong bleaching properties.

Water.—The discovery of the true composition of water was made by Cavendish in 1781, by burning known quantities of oxygen and hydrogen in a dry glass vessel, and observing that water was formed and deposited on the glass, and in quantity exactly equal to the weights of the gases which disappeared. He also found that these gases unite exactly in the proportion of two volumes of hydrogen with one of oxygen, and by weight, 1 to 8.

Pure water is colourless and transparent, and has neither taste nor smell. It is eminently neutral, having neither acid nor alkaline properties, and does not alter the nature of substances put into it. It often enters, however, into the composition of compounds; and many substances put into it have the property of decomposing it, and appropriating its elements.

The statement that water is entirely neutral, and having no action upon matters put into it, may appear doubtful to the practical dyer, as his daily experience teaches him, that the

waters he uses have a strong effect upon many of the dyes, and that certain kinds of water are better for some of his colours than others, which manifests a difference either in the condition or constitution of the water. This difference in water, experienced by dyers, depends upon foreign matters dissolved in it. It would therefore be a great object for the dyer to obtain pure water; or, if this is not practicable, to know, what the ingredients are that are in the water he is using, so that he may either counteract their effects and escape their consequences, or render them subservient to his purpose. The great practical importance of water to the dyer is, not only its neutrality, but also its solvent power. The cohesion of solid bodies is thus overcome, and the particles are diffused through those of the water, and so placed in the best possible condition for combining with the particles of other bodies, brought into proximity with them. We may illustrate this by taking two solid substances that have a strong affinity for each other, say tartaric acid and carbonate of soda; mix them together dry, there will be no apparent action; but if these substances be previously dissolved in water, and mixed, the action is violent and immediate. As may be supposed, therefore, it is its great solvent powers that gives us impure water.

Water is rendered pure by distillation. When caused to boil, it passes off as steam, and when steam is condensed by cooling, it is pure water, provided the impurities which were in the water before boiling do not fly off at a lower temperature than that of 212°. For instance, gaseous matters are expelled at lower temperatures, and alcohol, which boils at 180°, is also given off; but the impurities that are found in common water to affect the dyer are not given off, except these be in the water in great quantities, as in leys, in boiling which, some of the soda or potash is carried away with the steam, as already noticed.

The original source of all our water is from the surface of the ocean: it is evaporated, or vaporised, and carried through the atmosphere in the form of clouds, or in solution, and deposited upon the earth as dew or rain; but in this state it dissolves matters from the atmosphere, such as carbonic acid, ammonia, &c.; so that rain water, especially if near towns, is not altogether free of impurities. Nevertheless, when far from towns, or after having fallen for some time to purify the

air, rain is the purest water in nature, but the moment it touches the earth, it dissolves some solid matters, and becomes contaminated with the ingredients of the soil over or through which it passes; and these ingredients cause the differences experienced by dyers. The nature of the impurities depends upon the immediate source of the water, the nature of the soil or strata of earth through which it has passed, and as these substances act and react upon the dye-stuffs used, it becomes of the first importance that the dyer should fully comprehend the character and effects of the substances dissolved in the water he is using. These ingredients are generally lime, magnesia, alumina, potash, soda, iron, copper, sulphuric acid, hydrochloric acid, and carbonic acid. There are also other substances, which have been found in springs, in more minute quantities, but which we need not enumerate here, as they are not common; and even some of these given, such as copper, are not often present in waters used in the dye-house. These earthy substances are generally found in the water combined as sulphates, chlorides, or carbonates. There are also gases present in all waters, as atmospheric air, carbonic acid, sulphurous acid, &c. The last named gas is easily detected by the smell, and water could not be used for dyeing containing an appreciable quantity of it. Copper will not be present except in the vicinity of a copper mine, or a copper-ore vein, which would not be a fitting locality for a dye-house. Iron, as a sulphate, or chloride, is often present in very minute quantity; but when the quantity is considerable, the water is not good for many purposes; and, if the water is conveyed through lead pipes, or retained in leaden tanks, a small trace of lead may be detected, which is not only deleterious to the dyer's operations, but very destructive to health. One common definition of the quality of water is *hard* and *soft;* but this expression, so far as regards the dyer, is somewhat ambiguous, and is only useful when alkalies and soaps are to be used. Distilled water is soft and pure, and useful for all purposes of the arts; but a water may be soft and useful for bleaching and washing, and very deleterious in dyeing; and it may be hard, and yet good for dyeing most colours. Such a term, therefore, does not denote any particular kinds of impurities. If a piece of pure white soap be dissolved in alcohol, not so strong as to form a jelly, and a little of

this solution be dropped into water, if the soap *curdles* the water is hard; if not, it is soft. If hard, the ingredients are of an acid or an earthy nature, such as carbonic acid, carbonate of lime or iron, sulphate of lime, &c.; if soft, it may contain alkalies. The ingredients in the water are often so minute that the ordinary tests do not, for some time, detect them. The best mode of proceeding is to apply the soap test preliminarily, as a sort of guide;* next, to try the water with delicately-prepared test papers, and observe whether it has any acid or alkaline reaction, then take a gallon of the water and boil it down to a pint; put this into a narrow jar, and allow it to settle for a few hours; pour off the clear liquid into another vessel, and retain the turbid remainder for examination. The insoluble precipitate, if any, will most probably be carbonate and sulphate of lime, and a little iron. Carbonate of lime is held in solution as bi-carbonate; but the boiling decomposes this compound, one proportion of carbonic acid being given off, and the insoluble carbonate precipitates. The sulphate of lime is soluble only in small quantity, and a little is precipitated by boiling. To the precipitate add a few drops of hydrochloric acid, and the carbonate of lime and iron will dissolve with effervescence, while the sulphate will remain undissolved. A drop or two of gallic acid added to the acid solution will detect iron, by giving a black or bluish colour. A portion of this solution may be taken, and a little ammonia added to neutralize the acid; if lime is present, the addition of a little oxalate of ammonia will give a white precipitate.

The pint of water boiled down is now divided into five different portions, and put into small wine or test glasses.

To one portion is added a few drops of gallic acid, which, if iron be present, will, after standing some time, produce a bluish colour.

To another portion add a few drops of oxalate of ammonia, which will give a white precipitate if lime is present. This should be heated a little.

To a third portion add a few drops of phosphate of soda, and stir it well. After standing some time, if a white precipi-

* The soap test for water has been carried out to a great extent, and probably to general practical use, by Professor T. Clark. (See his papers in the *Chemical Gazette.*)

tate be formed, this will indicate the presence of magnesia.

To a fourth portion add chloride of barium; if a white precipitate is obtained, which is not re-dissolved by adding a little pure nitric acid, sulphuric acid is present.

To the fifth portion add nitrate of silver; if a white precipitate is formed, not re-dissolved by the addition of a little pure nitric acid, then hydrochloric acid is present.

These tests, and the nitric acid used, of course, must be perfectly pure, or no dependence can be placed upon the results.

If carbonic acid exists in the water, which it does very commonly in combination with a base, it will be known, as already intimated, by the effervescence caused by the addition of an acid; but it may exist free; and the best way to detect it, is to take a separate quantity of the water, without boiling, say a pint, and add to it a little clear lime water; if milkiness appear, carbonic acid is present, either free or as bi-carbonate of lime.

If blue litmus paper be reddened, there is free acid present in the water.

This manner of proceeding, which is very simple, is sufficient to give the dyer an idea of the impurities he has to contend with. Of course, the effects of each of these separately, or together, upon his dye-drugs, will also have to be studied; but this we refer to the separate heads under which they naturally fall. Should a more correct investigation be required, such as the exact quantities of each ingredient, this must be done by a regular course of analysis, which, we are afraid,. few practical dyers have the apparatus, or other means of making. However, with the tests referred to, a near approximation may be come at, by boiling the gallon of water to dryness, and carefully weighing the contents, which will give the whole solid matters in the gallon; and afterwards, by dissolving this in distilled water, pouring off the solution, and drying the insoluble portion, the quantity of soluble salts, which may be those of potash, soda, magnesia, &c., will be found. The water is tested for these and all the other ingredients, by the tests given. To the remaining insoluble part, a few drops of hydrochloric acid are added; and notice is taken if this produces effervescence. This acid solution is

then diluted with distilled water, and tested as above; if any thing remains insoluble, it is again dried and weighed, and the result will indicate the silica present. The following table, from Parke's Chemical Essays, a book well worth perusal by practical men, will be a guide to the testing of water:—

Test Used.	Will Detect.
Oxalates, or oxalic acid.	Lime, or its salts.
Litmus.	Uncombined acids.
Turmeric paper.	Alkalis and alkaline earths.
Chloride of platinum in alcohol.	Salts of potash.
Nitrate of silver.	Hydrochloric acid or chlorides.
Salts of barytes.	Sulphuric acid or sulphates.
Lime water.	Carbonic acid.
Acetate of lead.	Sulphuretted hydrogen in becoming black, or sulphates.
Chloride of lime.	Carbonated alkalies.
Polished iron.	Copper (is precipitated.)
Phosphate of soda.	Magnesia.

For the particular effects of some of these tests, the reader is referred to the articles upon these substances.

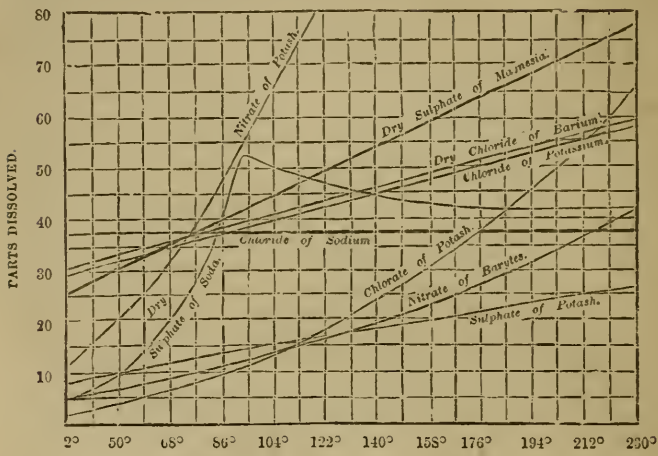
Water is used in the dye-house principally as a solvent; but its solvent property depends upon certain laws. The action being the mutual attraction between the solid and fluid, it becomes weaker as the attractions are satisfied. If, for example, we take a piece of white sugar of lead, and immerse one small point of it in water, the liquid is quickly drawn up into its pores, and adheres to the particles of the salt. If more water than is merely sufficient to wet the particles is allowed to enter, the solid particles of the salt break down and disappear in the water; in other words, the salt is dissolved. But this action of the water upon the salt is limited: it is very powerful at first, but the salt becoming diffused through the liquid, the action upon the solid decreases gradually, until the water gets satisfied, and will dissolve no more; the water is then said to be saturated.

An important point in dissolving salts may here be noticed. In dissolving quantities of crystallized salts, such as alum, sugar of lead, &c., the custom is to put the solid crystals into

a vessel, and pour water upon them; and a person keeps stirring until the whole is dissolved. This takes up much valuable time, and there is often a remainder of the salt not dissolved. If, instead of proceeding in this way, the quantity of water which it is necessary to use be put into the vessel, and the crystals of the salt be suspended upon the surface, the solution would proceed much more rapidly, and more economically, than any other way. As the particles of water take up the particles of the salt, they become heavier, and sink; other particles take their place, dissolve more of the salt, and sink in turn; so that the action of a constant current of liquid is kept up on the suspended crystals, and always of that portion of the liquid most capable of dissolving. When crystals of any salt are put into a vessel, and water poured over them and allowed to remain, they are a very long time in being dissolved; as the water surrounding the crystals becomes saturated, and incapable of dissolving more, and from its weight it remains at the bottom of the vessel. This may be beautifully illustrated by taking three tumblers filled with water, and adding to each an equal weight of crystallized sulphate of copper. In the one let the crystals rest at the bottom, stir the other constantly, and let the third be suspended upon the surface of the water, the action will be seen, and the difference in time appreciated.

In general, hot water dissolves more of a salt than cold water; but the relation of different dissolving powers of water, at different temperatures, and for different salts, is very curious. Some salts dissolve equally at all temperatures, such as common salt. Some salts dissolve least in cold water, and increase gradually as the water is heated; others, again, increase rapidly, until the water is at a certain temperature, and then become less soluble; while other substances, such as lime, dissolve most easily when the water is cold. Thus, 66 gallons water, at 32° Fah. dissolve 1 lb. lime; but it will take 75 gallons at 60° Fah., or 128 gallons at 212°, to produce the same effect; so that boiling water can contain only about the half of the lime that ice-cold water can. Thus, when lime water, at 60°, which is about the maximum heat of water in summer, is boiled, a quantity of lime is deposited as the heat increases. This is often experienced in the *raising* of chrome oranges.

The following table illustrates these remarks, and is of the greatest value to the dyer :—



It will be seen here that if a salt is dissolved in boiling water to saturation, and allowed to cool, a great quantity will be deposited either as crystals or powder ; also, if we wish to have a highly-saturated solution, there are certain temperatures better adapted for obtaining it than others. The best means is to use the salt dissolved in cold water, as above stated ; and the dyer, while he uses his stuff, as the salts of iron, alum, &c., should know that when he uses the full of a ladle, or pail, or small mug, he is taking exactly so many ounces or pounds of the salt, not so many measures, as is generally the case, without reference to the particular strength of the solution.

The following table of the quantity of a salt dissolved in a gallon of *cold* water at saturation, will be an example of this :—

Common salt,	$4\frac{1}{2}$lb. per gallon.
Sal-ammoniac,	$3\frac{1}{2}$ —
Sulphate of copper,	$4\frac{1}{2}$ —
Sulphate of iron,	7 —

Sulphate of zinc, ...$9\frac{1}{4}$ lb. per gallon.
Sulphate of nickel,.....$7\frac{1}{2}$ —
Sulphate of soda,.....$4\frac{1}{2}$ —
Alum, ...$1\frac{1}{2}$ —

Comparing this with the diagram above, it will be seen that double the quantity of some of these salts is dissolved in boiling water.

Besides the property for dissolving solid bodies, which we have been considering, water, as has been previously said, has also the property of dissolving gases, and holding them in solution. In this case, cold water is a more powerful solvent than hot. Some gases, if held in solution by water used in dyeing, would be very deleterious; and as many of these gases are often floating about in the dye-house, they may be absorbed by the water in small quantities, and be injurious, and the cause of the injury may not be known or thought of. The following are a few of these gases, and their solubility in water.

100 volumes, or cubic inches of water, at 60°, will dissolve about

253	volumes of	sulphuretted hydrogen,	weighing	93.6	grains.
438	,,	sulphurous acid,	,,	300.	,,
206	,,	chlorine,	,,	155·7	,,
100	,,	carbonic acid,	,,	47·2	,,
76	,,	nitrous oxide,	,,	75.	,,

Any of these gases, in the water, will affect colours, and they are all, to some extent, gases given off in the dye-house.

One gallon is equal to 277 cubic inches, so that each gallon is capable of holding in solution

259·3 grains of sulphuretted hydrogen.
189·7 grains of sulphurous acid.
431·3 grains of chlorine.
130·7 grains of carbonic acid.
273· grains of nitrous fumes.

Bin-oxide of Hydrogen.—Bin-oxide of hydrogen is a colourless liquid like water; it has a metallic taste, and bleaches almost instantly all organic coloured substances. Its preparation is difficult and expensive. It is obtained by the decom-

position of the bin-oxide of barium; the preparation of which is also difficult. There are so many *minute* precautions required for the preparation of the bin-oxide of hydrogen, that almost no description which our limits permit would enable the student to prepare it; these are all given in detail, by Thenard, the discoverer of the compound, in his "*Traite de Chemie*," (vol. I., 6th edition.)

Could there be any means of procuring it readily and cheap, its uses would be invaluable, both as a bleaching agent, and also for oxidizing, and many other operations in the arts. It is often referred to in proof that oxygen has bleaching properties as well as chlorine, a fact which will be noticed to some extent under that element.

Hydrogen combines with other elements besides oxygen, giving rise to important compounds, such as sulphuretted hydrogen, a gas we have just referred to, and others, which will be treated of under the separate elements with which it combines.

NITROGEN (N. 14.)

If a small vessel be floated upon water, with a piece of phosphorus in it, and this be set on fire, and a glass jar be inverted over it, as represented by the annexed figure, the flame is soon extinguished, and the water, when the air within the glass cools, rises into the jar. Let the whole stand until the white fumes in the glass disappear, the remaining air in the jar will be found to differ entirely from common air; a candle will not burn in it, and an animal put into it would very soon die. This gaseous substance is nitrogen. The atmosphere is composed of oxygen and nitrogen: and the burning phosphorous combines with the former of these gases, forming phosphorous acid, constituting the white cloud referred to, which is absorbed by the water after a little time. The rising up of the water into the jar is

to supply the place occupied by the oxygen consumed, and nothing but nitrogen remains.

This element was first called AZOTE—the life-destroyer—by its discoverer, Dr. Rutherford, from its not having the power of supporting life; but the name was afterwards changed to nitrogen, on account of its being found to be the basic constituent of nitric acid, (aquafortis.) Nitrogen has neither taste nor smell, and is rather lighter than oxygen. Its use in the atmosphere is supposed to be for diluting the oxygen; but there is no doubt that other important purposes are served by its presence in the air, although we may be ignorant of them, as it forms an essential constituent of animals and vegetables, and also of many mineral productions. Nitrogen is peculiar for what are termed *inert* or *negative* properties. We cannot cause it to combine directly with any other element, as we do oxygen and hydrogen, or hydrogen and chlorine; nevertheless, it combines with a number of elements, when their compounds are being decomposed.

With oxygen, nitrogen forms a variety of interesting compounds, already alluded to (page 24), but which we will here notice more in detail, particularly those more commonly met with. As already remarked, the atmosphere is a mixture of nitrogen and oxygen, found to be in very nearly the same proportions under all circumstances and at all places, not in chemical union, but maintained in equal mixture by the principle of diffusion. There are a variety of methods for ascertaining the proportions of oxygen and nitrogen in the air: the one just described, the burning of phosphorus in an inverted jar over water, will suffice as an example. The results of careful investigations into this subject give as the constitution of the atmosphere in 100 parts:—

21 Oxygen.
79 Nitrogen.

But, from the constant evaporation of water from the sea and surface of the earth, and the production, by many causes, of carbonic acid gas, which finds its way into the atmosphere, the air always contains a small portion of those ingredients, which, being taken into account, makes the composition—

Oxygen, ...20.
Nitrogen,.....79.

Vapour of water,.....	0·9.
Carbonic acid,.....	0·1.
	100·0

The dyer cannot fail to have observed a thin crust of solid matter upon the surface of his lime solution, bleaching liquor, and blue vats. This crust is the carbonate of lime, and is caused by the carbonic acid in the air combining with the lime, and forming an insoluble carbonate. The presence of this gas in the air has no deleterious effects in the dye-house, so far as we know, except its combining with caustic alkalies, if exposed, and deteriorating them.

The oxygen of the atmosphere plays a very prominent part in the dye-house, and the knowledge of the true constitution of the air will make many of these phenomena better understood. This gas not being in chemical union with the nitrogen, there is no chemical force retaining and preventing it from acting upon other bodies, when brought under its influence.

The principal compounds formed between nitrogen and oxygen are—

Protoxide of nitrogen, ...	NO.
Deutoxide of nitrogen,.....	NO_2.
Nitrous acid, ...	NO_3.
Peroxide of nitrogen, ...	NO_4.
Nitric acid, ...	NO_5.

Some of these being of no known importance in the dye-house, we need do little more than refer to the condition in which they may be found.

Protoxide of Nitrogen is a gaseous body, and is easily obtained by distilling nitrate of ammonia in a retort, as described for obtaining oxygen (page 37), and collecting the gas as it escapes over water. It is known under the appellation of *laughing gas.*

Binoxide of Nitrogen is also a gaseous body, and is evolved when metals are being dissolved in nitric acid. When dissolving iron or copper in nitric acid, in open vessels, as is done for the preparation of mordants, a dense red gas is seen to escape during the process. This red gas is produced by the binoxide of nitrogen combining with the oxygen in the atmosphere, and forming a peroxide; but when the metal is

dissolved in a retort, or other close vessel, as described for hydrogen, and the gas collected in a glass jar, it is found perfectly colourless. The following is the reaction which takes place when a metal is being dissolved in nitric acid and oxide of nitrogen evolved. Every three proportions of metal require four proportions of acid, one of which is decomposed according to the following formula, supposing copper to be the metal dissolved:—

$$3\ Cu + 4\ NO_5 = 3\ Cu\ O\ NO_5 + NO_2.$$

But, according to the theory of salt radicals (page 33), the reaction is the following:—

$$3\ Cu \times 4\ NO_6H = 3\ Cu\ NO_6 + 4\ HO,\ NO_2.$$

According to either view of the reactions which take place, it will be observed that the proportions are the same, which may enable the dyer to guide himself in these substances when making nitrates of iron or copper.

Nitrous Acid.—This acid is prepared by taking four volumes of the binoxide of nitrogen, adding to them one volume of oxygen, and exposing this mixture to a low degree of cold: the gases, under these circumstances, unite, and form a greenish-coloured liquid, which is nitrous acid. As may be supposed, from the manner in which it is prepared, this substance is very volatile. If thrown into water it is decomposed. But it can be obtained by several means, in combination with bases, such as potash, soda, lead, &c., with which it is more stable.

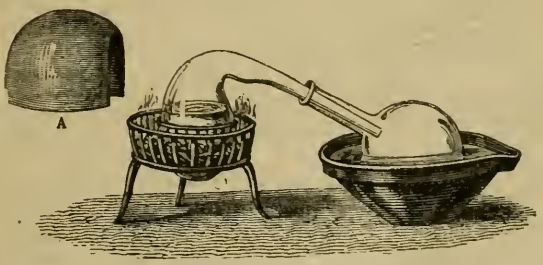
Peroxide of Nitrogen.—This compound is formed when the binoxide of nitrogen is allowed to escape into the atmosphere, and constitutes the red fumes observed when dissolving iron or copper in nitric acid. It is also obtained by distilling nitrate of lead in a retort, and allowing the fumes to pass into a bottle or flask kept cool by placing it in a freezing mixture, such as snow and salt. It condenses in this vessel, and forms a reddish-yellow liquid, which, however, passes off as gaseous fumes, by the slightest elevation of temperature. These fumes are very corrosive: they are fatal to animal and vegetable life and rapidly destroy all colours, and also the fibres of the cloth or yarn exposed to their action. The dissolving of metals in nitric acid should, there-

fore, never be carried on within or near the dye-house, or any place where goods are exposed. We have seen a little inattention to these precautions destroy the labour of several days, and this, too, when the destructive agent was hardly perceptible to the senses, although its odour is amongst the most easily detected of gaseous compounds. This gas is also very suffocating and hurtful to health, and care should be taken that it is not breathed. It is its presence in nitric acid which gives that acid the reddish-brown colour which the aqua-fortis of commerce often has.

Nitric Acid.—This acid exists abundantly in nature, in combination with other substances forming nitrates. We have said before that nitrogen and oxygen do not combine directly in the same manner as oxygen and hydrogen. There is no doubt, however, that the nitric acid which is found united with bases in nature, has been the result of the union of the oyxgen and nitrogen of the atmosphere. When a quantity of hydrogen is mixed with nitrogen in an open vessel and ignited, it burns rapidly in contact with the oxygen of the air, forming water; and the water thus formed is found to contain nitric acid. If electric sparks be passed through air, confined in a vessel above a solution of an alkali, a portion of the alkali is converted into a nitrate. Rain which falls during a thunderstorm, almost always contains nitrate of ammonia. Ammonia is always being given into the air by the decomposition of animal and vegetable substances, and absorbed by the watery vapour; so that when electric currents pass through the air during a thunderstorm, the nitric acid formed combines with this ammonia, forming a nitrate. In warm climates, where electric currents are abundant, the quantity of ammonia in the air is considerable; the formation of nitrate of ammonia is, therefore, proportionably great; and this, being washed down by the rain into porous limestone soils, is decomposed by the nitric acid combining with the lime and also with potash and soda, which are general constituents of soils, forming nitrates with these bases, and the ammonia is accordingly liberated, either to be given to the air again, or taken up by plants, as a constituent of their food. In this way, immense beds of nitrates have been formed in the East Indies and in South America. In Chili and Peru, there are found large deposits of nitrate of soda upon the surface of the

soil. Great quantities of nitrate of potash and soda are imported from these localities for the various manufacturing purposes of this country, where they are now extensively applied. The nitrate of lime and other earths, are converted into nitrate of potash, by mixing them with carbonate of potash, before sending them to this country.

Nitric acid is prepared from the nitrate of potash or soda, by decomposing it with sulphuric acid. This may be done, on a small scale, by putting a little of any of these salts into a retort, adding some sulphuric acid, and then applying heat. The beak of the retort is inserted into a receiver, which must be kept cool by causing cold water to drop upon it. The arrangement of the apparatus is indicated by the annexed figure.



At the beginning of this experiment, red fumes of peroxide of nitrogen come off; but soon after a colourless liquid is seen to distil over, and drop into the receiver—this is nitric acid. The reaction which takes place may be represented by the following formula.

$$Na\,NO_6 + SO_4H = Na\,SO_4 + NO_6\,H.$$

Nitrate of soda is now more generally used than potash, being cheaper, and having a lower combining equivalent, more nitric acid is obtained from a given weight. Thus, 100lbs. of nitrate of potash give 62lbs. of acid; while 100lbs. of nitrate of soda would give 74lbs. The best proportion of sulphuric acid to use with nitrate of potash is 2 equivalents, whereas less suffices with nitrate of soda.

Nitric acid is generally prepared, on the large scale, in iron cylinders, placed so that a fire plays round them. Into these

cylinders are put the materials; and the acid vapours which are distilled over are conveyed to the condensing apparatus by glazed earthenware pipes.

The nitric acid of commerce has generally a light-brown colour, caused, as before stated (page 52), by having a little peroxide of nitrogen in it. Sir H. Davy drew out the following table of proportions of nitrous gas contained in this acid, from its shades of colour. Thus, in 100 parts—

Colour.	Real Acid.	Water.	Peroxide of Nitrogen.
A pale yellow has	90·5	8·3	1·2.
A bright yellow has	88·9	8·1	2·9.
A dark orange has	86·8	7·6	5·5.
A light olive has	86·	7·5	6·4.
A dark olive has	85·4	7·5	7·4.
A bright green has	84·8	7·4	7·7.
A blue green has	88·6	7·4	8·

This table must be considered to refer only to strong acid, for the colour is changed by dilution. Thus, when water is added to the dark orange-coloured acid, it changes it to a greenish-yellow.

Exposure to the sun's light produces change of colour, by decomposing the acid, and liberating peroxide of nitrogen which remains dissolved in the acid. A little oxygen gas is, at the same time, evolved; and, if the bottle is stoppered, will either drive it out or burst the bottle, a fact too often experienced. The great effect of light upon this acid may be tried by placing a little of the colourless acid in the rays of the sun, and observing the change that follows; this will show the propriety of keeping nitric acid always in the dark. Neither should it be exposed to the air, by leaving the stoppers out of the bottles or carboys, as it thereby loses its strength rapidly.

The nitric acid, formed as we described, is often contaminated with iron from the retorts, and also with sulphuric and hydrochloric acids, from a little common salt and other impurities being in the *nitre* used. It is purified from these matters by redistilling in glass retorts. The acid coming off first in the distillation contains some hydrochloric acid; then nothing but pure nitric acid passes over, until nearly three-fourths of this acid is distilled. But if the operation be

pushed further, there is danger of impurities passing over. Of course, what remains in the retort contains the impurities.

Sometimes the quantity of impurities in the nitric acid of commerce is very considerable, and very deleterious to the dyer. The general test applied to this acid in the dye-house is the specific gravity, taken by Twaddell's hydrometer; but density is often given to the acid by dissolving a little *nitre* in it, or adding sulphuric acid. We have seen nitric acid, with 8 per cent. of sulphuric acid, giving it a high specific gravity. We have also seen it with as much as 5 per cent. hydrochloric acid. The presence of either of these acids is disadvantageous for the preparation of many of the mordants, as will be noticed under the proper heads.

When nitric acid contains *nitre*, or any other salt dissolved in it, the impurity may easily be detected by evaporating to dryness a little of the acid, either upon a piece of glass or a porcelain plate; when the acid is pure, no residue is left.

The presence of sulphuric acid is detected by diluting a small portion of the acid with four or five times its volume of distilled water, and adding a little solution of nitrate of barytes, which will give a white precipitate if sulphuric acid is present.

Hydrochloric acid, or chlorine, may be detected by adding a little nitrate of silver to the dilute acid, which will also give a white precipitate if any hydrochloric acid be present.

Iron is detected by adding a little gall water to the dilute acid, a bluish-black colour then appears. Or, if on evaporating a small portion of the acid there is a residue of a brown colour, it indicates the presence of iron.

After having tested for the presence of these substances, and finding the acid pure, or nearly so, then the specific gravity may be taken, as a further certainty of the value of the acid. This varies much with the acids of commerce, but is generally about 1·300 = 60° Twaddell, although it may be made as high as 1·500 = 100° Twaddell. Nearly all the hydrometers used in this country are those known as Twaddell's, which is an arbitrary scale. The true specific gravity may be reduced to Twaddell's, by dividing the fractional figures by 5, as will be observed from the above. But in trying the acids by a Twaddell's hydrometer, the above rule is to be reversed: we then multiply the degree of Twaddell by 5, add 1000, and divide the sum by 1000. Thus, supposing

the specific gravity to be 60° of Twaddell, then $60 \times 5 = 300$; which, increased by 1000, becomes 1300; and this, divided by 1000, gives 1·300, the true specific gravity. Or say 64°, Twad. which is a common number, then—$(64 \times 5 = 320) + 1000 = 1{\cdot}320$ specific gravity. The following table shows the quantity of acid in 100 parts, which may be called ounces or pounds, or any weight convenient, according to the true specific gravity.

TABLE OF THE QUANTITY OF ACID IN 100 PARTS BY WEIGHT.

Specific Gravity.	Acid in 100 parts.	Specific Gravity.	Acid in 100 parts.
1·5000	100	1·2947	50
1·4980	99	1·2887	49
1·4960	98	1·2826	48
1·4940	97	1·2765	47
1·4910	96	1·2705	46
1·4880	95	1·2644	45
1·4850	94	1·2583	44
1·4820	93	1·2523	43
1·4790	92	1·2462	42
1·4760	91	1·2402	41
1·4730	90	1·2341	40
1·4700	89	1·2277	39
1·4670	88	1·2212	38
1·4640	87	1·2148	37
1·4600	86	1·2084	36
1·4570	85	1·2019	35
1·4530	84	1·1958	34
1·4500	83	1·1895	33
1·4460	82	1·1833	32
1·4424	81	1·1770	31
1·4385	80	1·1709	30
1·4346	79	1·1648	29
1·4306	78	1·1587	28
1·4269	77	1·1526	27
1·4228	76	1·1465	26
1·4189	75	1·1403	25
1·4147	74	1·1345	24
1·4107	73	1·1286	23
1·4065	72	1·1227	22
1·4023	71	1·1168	21

Specific Gravity.	Acid in 100 parts.	Specific Gravity.	Acid in 100 parts.
1·3978	70	1·1109	20
1·3945	69	1·1051	19
1·3882	68	1·0993	18
1·3833	67	1·0935	17
1·3783	66	1·0878	16
1·3732	65	1·0821	15
1·3681	64	1·0764	14
1·3630	63	1·0708	13
1·3579	62	1·0651	12
1·3529	61	1·0595	11
1·3477	60	1·0540	10
1·3427	59	1·0485	9
1·3376	58	1·0430	8
1·3323	57	1·0375	7
1·3270	56	1·0322	6
1·3216	55	1·0267	5
1·3163	54	1·0212	4
1·3110	53	1·0159	3
1·3056	52	1·0106	2
1·3001	51	1·0053	1

The presence of free nitric acid in a solution is easily ascertained by the production of red fumes when a metal is put into it, such as iron or copper; or by adding to the substance supposed to contain it a drop of sulphate of indigo, and heating the solution to the temperature of boiling: the indigo will be discoloured if nitric acid is present. But if the acid is combined with a base, such as soda or potash, this test will not answer. In that case, the best mode of proceeding is to put a little sulphuric acid into the liquid suspected, and then to add a crystal of sulphate of iron, (copperas.) If nitric acid be present, a ring of an olive-brown coloured liquid will form round the crystal as it dissolves; and by applying heat, the well-known smell of nitrous fumes is felt. By these simple means, the dyer can easily ascertain if nitric acid is present, either free or combined, in any compound with which he is working.

The action of nitric acid on the different metals will be noticed under the proper heads; but one remarkable circumstance connected with this class of action must have been observed by most dyers when dissolving iron, namely, that

on putting the iron into the acid, it often remains without any action: when this occurs with new acid, complaints are made that the acid is bad or weak, or that something is wrong that prevents it dissolving the iron; and not unfrequently have we seen carboys of acid returned on this account. Recently we had a sample of such acid, and found it to stand in specific gravity 1·425; and to contain a mere trace of salts and sulphuric acid, with 0·1 per cent. of hydrochloric acid. It was a strong and comparatively pure nitric acid, which was its fault. The cause of the iron not being acted upon, is from a condition which iron is known to assume, termed the *passive state;* in which condition acids do not act upon it. Strong and pure nitric acid places the iron in this state, and therefore it is not dissolved till the acid is diluted, or heat applied. We cite the above case as an illustration of the value a little attention to chemical principles would be in many dye-houses, not only in saving money, but also preventing the manufacturer being *necessitated* either to adulterate or dilute his acid, in order to preserve a good and profitable customer.

Nitric acid is very corrosive, from which property it was named aquafortis. It destroys all organic bodies, both vegetable and animal. It converts vegetable matter into oxalic, carbonic, and several other acids. Animal substances are acted upon by this acid, producing the yellow-coloured compounds, observed when it comes in contact with the skin or nails. It should be used at all times with great care.

Ammonia.—Nitrogen combines with hydrogen, and forms a very important compound, ammonia; composed of one proportion of nitrogen and three hydrogen, NH_3. Ammonia is abundantly obtained from the destructive distillation of organic matters containing nitrogen, such as bones, horns, skins, blood, and other animal matters. It is also obtained as a product in the gas-works. When animal matters are decomposed by burning or putrefaction, ammonia is formed, and produces the disagreeable smell which these operations generally give.

The ammoniacal liquors obtained from gasworks, or by distilling animal matters, are saturated with hydrochloric acid, which converts the ammonia into hydrochlorate of ammonia, (sal-ammoniac,) which crystallizes in a very impure state. These crystals are collected and put into iron pots, set in a

furnace lined with fire tiles, and having a large cover or head of lead fitted to them. Fire is applied to the pots, the sal-ammoniac sublimes and collects as a crust upon the leaden top, from which it is removed from time to time.

Ammonia is prepared by mixing equal parts of slaked lime and sal-ammoniac, and applying heat. The lime combines with the hydrochloric acid, and the ammonia passes off as a gas, and is conducted by a pipe into water, with which it combines, and forms liquid ammonia.

Ammonia, long known as hartshorn, is a strong alkali, and has a very pungent, sharp smell. It is an exceedingly valuable re-agent in the laboratory, both as a test and for making many interesting salts by combination with acids, the greater number of which are volatile. These salts are, however, not much used in the dye-house. Ammonia is sometimes used for the preparation of archil, for bringing out the colour. Its action upon the colouring matter of the woods is very powerful. It is the presence of ammonia and some of its salts in urine, which gives that fluid the peculiar properties for which it is used in the dye-house—as a cleansing agent for woollen, and for *raising* the colour of a decoction of log-wood.

Nitrogen also combines with some of the other elements, forming compounds more or less interesting according to their applications, some of which will be noticed when treating of the elements with which these combinations take place.

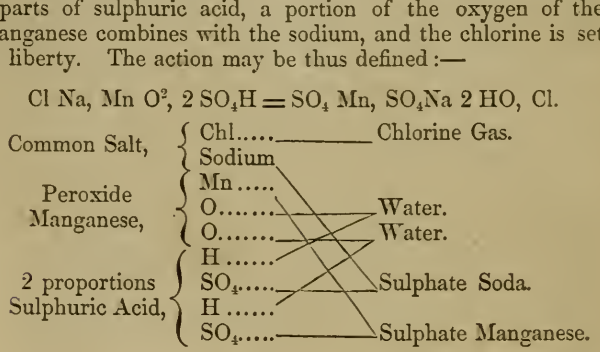
Chlorine (Cl 36).

Chlorine was discovered by Scheele, in 1774, and was called by him *dephlogisticated* muriatic acid. About eleven years after this, Berthollet considered that he had found it to be a compound of muriatic acid with oxygen, and hence termed it *oxygenized muriatic acid*—a name which was afterwards contracted into *oxymuriatic acid.* In 1811, Sir H. Davy discovered it to be a simple or elementary substance, and gave it the name of chlorine, from its having a greenish-yellow colour. Chlorine has a very strong, suffocating smell, occasions violent coughing and debility, and gives an astrin-

gency to the mouth: therefore breathing it ought to be avoided as much as possible.

Chlorine exists in nature in large quantities, in combination with other elements, particularly sodium, forming chloride of sodium (common salt). It is from this source that it is prepared for use in the arts. If we mix about 8 parts of salt with 6 parts of black oxide of manganese, and add to this about 3 parts of sulphuric acid, a portion of the oxygen of the manganese combines with the sodium, and the chlorine is set at liberty. The action may be thus defined:—

$$Cl\,Na,\ Mn\,O^2,\ 2\,SO_4H = SO_4\,Mn,\ SO_4Na\ 2\,HO,\ Cl.$$



Chlorine combines with almost all the elements, and forms with them a series of compounds as numerous as they are important. Its power of combining with, and decomposing, colouring substances is remarkable, and has given it a prominent standing in the arts. It combines with oxygen in various proportions, giving origin to several compounds, both useful and interesting to the dyer. These, as the following list shows, have all acid properties:—

Hypochlorous acid, ...Cl O.
Chlorous acid, ...Cl O_4.
Chloric acid, ...Cl O_5.
Perchloric acid, ...Cl O_7.

Hypochlorous Acid.—This is a very unstable compound, supposed to be connected with many of the operations of bleaching. It may be prepared by diffusing some red oxide of mercury in a little water, and then introducing it into a bottle previously filled with chlorine gas. The chlorine is rapidly absorbed, and combines with both the mercury and oxygen. It pro-

duces, with the former, an insoluble oxychloride, and with the latter it forms hypochlorous acid, which is in solution in the water. This solution has a yellow colour, smells like chlorine, and bleaches powerfully; but it cannot be kept for any length of time, even in the cold, but passes into chloric acid. Hypochlorous acid combines with alkaline bases, and forms hypochlorites, which also possess bleaching powers. It is generally supposed that when chlorine gas is passed through solutions of the alkalies, such as potash and soda, a similar decomposition takes place as that described of the oxide of mercury, and that the hypochlorite of the alkali is the bleaching salt formed. This salt is decomposed by heat.

Chlorous Acid may be prepared by adding strong sulphuric acid to chlorate of potash. The process is a dangerous one, and we would not advise any student to try it, especially as neither the acid nor its salts are of any great importance. The acid is a gaseous body of a yellow colour: it combines with bases, and forms salts termed chlorites. These also possess bleaching powers, and are very unstable.

Chloric Acid.—This acid is not of any value in a separate form, and is obtained with difficulty; but it is easily enough obtained in combination. When chlorine gas is passed through a solution of caustic potash, it is rapidly absorbed. This, by standing some time, or by the application of a little heat, becomes converted into a mixed salt of chloride of potassium and chlorate of potash. Thus—

$$6\ Cl,\ 6\ KO = 5\ Cl\ K,\ Cl\ O_6\ K.$$

The chlorate of potash being less soluble than the chloride, it is easily separated by crystallizing. Chlorate of potash has very strong detonating powers, and should be used with great care by the student, especially when mixing it with any other substance, as these are often explosive. It is extensively used for lucifer matches. We are not aware that this salt is used to any extent as yet in the dye-house; but from the property it possesses of giving off oxygen easily, it may be made very useful in many operations, where oxydation is an object. It is becoming extensively used in calico print-works.

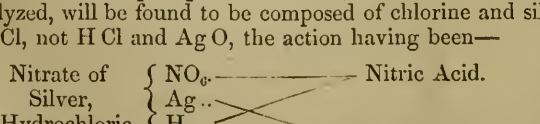
Chloric acid combines with other bases besides potash. These compounds were for a long time, and are occasionally still termed *hyper-oxymuriates.*

Hyperchloric Acid is formed from the chlorate of potash. It may be obtained in combination with potash, by acting upon the above-named salt with nitric acid, and putting the whole afterwards into a small portion of boiling water: on cooling, the hyperchlorate of potash separates in crystals. The acid may be separated from the base by boiling it with fluosilicic acid, when the hyperchloric acid remains in solution. This acid, or its salts, has no bleaching properties. It is an interesting compound in its chemical relations, but not yet of much importance to the arts.

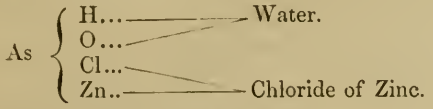
Hydrochloric Acid.—Chlorine unites with hydrogen, and forms an important compound, hydrochloric acid (muriatic acid.) It is a gaseous substance, very soluble in water, in which state it is used, and has been known since a very early period in history under the names of *marine acid, spirit of salt*, &c. Hydrochloric acid is easily obtained by the action of sulphuric acid on common salt. It is prepared on the large scale, by pouring vitriol on common salt, in a furnace prepared for the purpose; the fumes passing off are absorbed by water, which thus becomes liquid hydrochloric acid, weak at first, but it is afterwards concentrated by distillation. The reaction going on during the preparation may be thus represented:—

$$NaCl\ SO_4\ H = NaSO_4,\ Cl\ H.$$

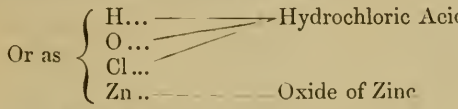
The sulphuric acid is generally used in a diluted state, so that there is always a great quantity of watery vapour passing off with the gas. This acid combines with bases, and forms a series of important salts. That from which it is obtained, viz. chloride of sodium, is a good example. It is matter of inquiry, as we have before stated, whether this acid be capable of combining with bases, or if it is not decomposed, and water formed along with the chloride of the base. As for instance, if hydrochloric acid be added to nitrate of silver, a white precipitate is formed, which, if collected and analyzed, will be found to be composed of chlorine and silver. Ag Cl, not H Cl and Ag O, the action having been—



But if we dissolve a piece of zinc in hydrochloric acid, and evaporate to dryness, we get a white powder, which, on analysis, will give zinc, chlorine, and water, in single equivalents. The question then is, whether these elements do not arrange themselves—



Forming chloride of zinc with water.



Forming Muriate of Zinc.

We have, at the risk of repetition, introduced this here, knowing that there is confusion in these names among practical men, and have only again to state that all muriates should be properly termed chlorides. Some authors, to make a distinction, call salts that are in union with water, such as the zinc salt above, *muriates*, and only dry salts, as that of silver, *chlorides*. The terms, when thus understood, may be used synonymously, so that no confusion need occur on that head. When hydrochloric acid is exposed to the air, it emits white fumes, which is hydrochloric acid gas with a little watery vapour; hence exposure weakens the acid, and should be avoided as much as possible in the dye-house. This gas, besides, corrodes rapidly any substance it comes into contact with, and destroys colours. It is a colourless acid when pure, but exposure to the light renders it of a yellow colour; strong sunshine decomposes it, and, of course, should be avoided.

The common impurities in this acid are iron, sulphuric acid, and sulphurous acid. The iron may be detected by adding to a little of the dilute acid a drop of gallic acid. Sulphuric acid may be detected by adding a solution of chloride of barium to some of the acid diluted with distilled water: which gives a white precipitate with sulphuric acid. If the clear solution filtered from this test be boiled with a little

nitric acid, any sulphurous acid will be converted into sulphuric acid, which will be precipitated by the barium, and its presence detected. Different chloride salts, such as common salt, are sometimes added to hydrochloric acid, to give it weight and specific gravity. This admixture may be detected by evaporating a little of the acid in a small porcelain saucer, or on a piece of glass, and seeing if any residue be left. Pure acid should leave nothing; if residue of a brown colour, it indicates iron. If the acid is found by these tests to be pure, then the specific gravity may taken to ascertain its strength. The following table will serve as a guide:—

Acid of Spec. Grav. 1·20 in 100 parts.	Specific Gravity.	Muriatic Acid.
100	1·2000	40·777
99	1.1982	40·369
98	1·1964	39·961
97	1·1946	39·554
96	1·1928	39·146
95	1·1910	38·738
94	1·1893	38·330
93	1·1875	37·923
92	1·1857	37·516
91	1·1846	37·108
90	1·1822	36·700
89	1·1802	36·292
88	1·1782	35·884
87	1·1762	35·476
86	1·1741	35·068
85	1·1721	34·660
84	1·1701	34·252
83	1·1681	33·845
82	1·1661	33·487
81	1·1641	33·029
80	1·1620	32·621
79	1·1599	32·213
78	1·1578	31·805
77	1·1557	31·398
76	1·1536	30·990
75	1·1515	30·582
74	1·1494	30·174
73	1·1473	29·767

Acid of Spec. Grav. 1·20 in 100 parts.	Specific Gravity.	Muriatic Acid.
72	1·1452	29·359
71	1·1431	28·951
70	1·1410	28·544
69	1·1389	28·136
68	1·1369	27·728
67	1·1349	27·321
66	1·1328	26·913
65	1·1308	26.505
64	1·1287	26·098
63	1·1267	25·690
62	1·1247	25·282
61	1·1226	24·874
60	1·1206	24·466
59	1·1185	24·058
58	1·1164	23·650
57	1·1143	23·242
56	1·1123	22·834
55	1·1102	22·426
54	1·1082	22·019
53	1·1061	21.611
52	1·1041	21·203
51	1·1020	20·796
50	1·1000	20·388
49	1.0980	19·980
48	1·0960	19·572
47	1·0939	19·165
46	1·0919	18·757
45	1·0899	18·349
44	1·0879	17·941
43	1·0859	17·534
42	1·0838	17·126
41	1·0818	16·718
40	1·0798	16·310
39	1.0778	15·902
38	1·0758	15·494
37	1·0738	15·087
36	1·0718	14·679
35	1·0697	14·271
34	1·0677	13·863

Acid of Spec. Grav. 1·20 in 100 parts.	Specific Gravity.	Muriatic Acid.
33	1·0657	13·456
32	1·0636	13·049
31	1·0617	12·641
30	1·0597	12·233
29	1·0577	11·825
28	1·0557	11·418
27	1·0537	11·010
26	1·0517	10·602
25	1·0497	10·194
24	1·0477	9·786
23	1·0457	9·379
22	1·0437	8·971
21	1·0417	8·563
20	1·0397	8·155
19	1·0377	7·747
18	1·0357	7·340
17	1·0337	6·932
16	1·0318	6·524
15	1·0298	6·116
14	1·0279	5.709
13	1·0259	5·301
12	1·0239	4·893
11	1·0220	4·486
10	1·0200	4·078
9	1·0180	3·670
8	1·0160	3·262
7	1·0140	2·854
6	1·0120	2·447
5	1·0100	2·039
4	1·0080	1·931
3	1·0060	1·224
2	1·0040	0·816
1	1·0020	0·408

Chloride of Nitrogen.—Chlorine combines with nitrogen to form NCl_3, which is one of the most explosive compounds known. It is a heavy liquid substance, and, from its dangerous properties, cannot be of any use to the dyer.

Chlorine also combines with some of the other non-metallic elements, such as phosphorus, sulphur, carbon, &c., and

forms compounds, some of which are interesting in a chemical point of view, but not in respect to their practical use in the dye-house. The chlorides of the metals, however, are some of them important, and will be described as they occur, under the metals.

The great use of chlorine in the dye-house is as a bleaching agent—into the consideration of which we will now enter a little more in detail.

While treating of light (page 12), we had occasion to notice the necessity of goods being a pure white previous to being dyed any light *fancy** shade; otherwise the natural yellow colour of the goods, whether cotton, silk, or woollen, would interfere with the particular shade wanted. If, for example, the shade required be a light pink upon cotton, and a little safflower, the stuff used for dyeing pink, be put upon it, unbleached, the resulting colour would not be a pink, but a shade intermediate between a salmon and a brick colour, from the yellow ray reflected from the cotton mixing with the red reflected from the dye. We must, therefore, before dyeing a light pink, get rid of these yellow rays, and this is effected by the process of bleaching. Hence, the dyer must, of necessity be also a bleacher.

Where and when the practice of bleaching cloth first began, we have no account; but we may reasonably suppose that, as soon as man became so far civilized as to manufacture clothing, that the constant exposure of that clothing to the atmosphere, and occasional washing, would naturally suggest the idea of bleaching. However, we know that bleaching is of very ancient origin, mention being made of it in the oldest books extant. What was the nature of the process practised in these early times is not clear; but from the earliest description to the close of last century, no other process was known but alternate boiling, washing, and exposure to the atmosphere, a process which required a number of months to complete; but, since the application of chlorine to this purpose, an application which, as Professor Graham observes, "is one of the most valuable which chemistry has presented to the arts," the process is completed in a few days; nay, for the most of dyeing operations, in a few minutes.

As many are now unacquainted with the routine of the

* This is a technical term for fugitive colours, or colours not fast.

process of bleaching previous to the introduction of chlorine, it may be worth while to give a short description of it, to illustrate the advantages obtained from the application of science to the arts. The first operation was that of steeping, which was merely immersing the yarn in hot water or cold alkaline leys. When water was used, the steeping lasted for three or four days, but with alkaline leys forty-eight hours were sufficient; the goods were then washed, and boiled in an alkaline ley for four or five hours; washed and exposed on the grass for two or three weeks; again boiled or *bucked*, which is a technical term for boiling; washed and *crofted*, a technical term for exposing on the grass, as before. These alternate operations of bucking, washing, and crofting, were generally repeated four or five times, each time reducing the strength of the alkaline leys in which the bucking was performed.

The next process was that of souring, which, till nearly the middle of last century, consisted in steeping the goods for several weeks in soured butter-milk. This process was much shortened by Dr. Home, who suggested the use of sulphuric acid (vitriol) instead of milk; and twelve hours, with a sour of this acid, were sufficient.* After the first souring, the operations of boiling, washing, souring, and crofting were repeated in regular rotation, until the yarn came to a good colour, and was considered perfectly clear. A quantity of soap was generally used in the last operations of boiling. The number of times these operations were repeated varied according to the quality of the goods; linen was seldom finished in less than six months, and cotton goods varied from six weeks to three months.

Various opinions were advanced to explain the nature of the chemical changes induced during these operations; but such opinions could be only hypothetical so long as the composition of the atmosphere and of water were not known, two substances which acted a very prominent part in these operations, and also while we were ignorant of the nature of the colouring matter upon the goods, and its composition. We have already given the composition of water and air, but the composition of the colouring matter upon cotton, &c. has not as yet been very accurately ascertained. Its properties are neutral, and of a resinous nature, from which, as a general principle, we

* Home on Bleaching.

may safely say, that the neutral is composed of hydrogen and carbon with oxygen; and, from the composition of resinous matters in general, it will be composed of hydrogen and carbon, and soluble in alkalies and water, and therefore mostly all taken out by steeping and boiling. These resinous and colouring matters do not form a part of the cotton, but mechanically adhere to it, so that substances may act upon and decompose them without in the least destroying the cotton; indeed, from a number of experiments, cotton is found as strong when deprived of these substances as before.

In boiling cotton yarn in water alone, it loses considerably in weight; different qualities of cotton varying in this respect; fine qualities lose least. From a number of experiments, made expressly to ascertain this point, and with various qualities of cotton, the average of loss may be taken at 5 per cent. of the weight of the cotton.

In order to ascertain the chemical changes which take place when goods are bleached in the air, M. Berthollet, finding that those seasons when most dew was deposited, were the most effective upon the colour, examined the dew which falls from the atmosphere, and also that which transpires from the grass, and found both to contain a sufficient quantity of oxygen to destroy the colour of turnsole paper.* What errors led to these results we do not know, for although dew did contain oxygen, it would not give it acid properties to redden turnsole paper. Or whether M. Berthollet considered the bleaching property of dew owing to its having free oxygen, or to this acid property, we do not know, not having seen the original details. Could we suppose the formation of peroxide of hydrogen (page 47), the effects would be easily explained.† The theory of croft bleaching has been explained variously as follows:—

1. The oxygen of the atmosphere combines with the colouring matter of the cotton, forming a new substance capable of solution in water or alkalies, and comes off by washing or boiling; or it combines with some of the elements of the colouring matter, such as the carbon, forming carbonic acid gas, which escapes into the air, or with the hydrogen, and forms water; those elements which are left, form either colourless substances, or substances soluble in the next operation.

* Parke's Chemical Essays. † See Ozone.

2. The oxygen combines directly with the colouring matter, forming a permanent and colourless oxide.

3. The water acts otherwise than being merely a solvent; that it, or one of its elements, combines with the colouring substance producing the effects noticed in the first proposition. Hence dew being pure and free from any admixture which might retard this union, is better fitted for bleaching; consequently, in seasons when most dew is deposited, the bleaching process will be accelerated. Which of these theories is the true one, we cannot say; but we know that light facilitates the process of bleaching, and this circumstance, we think, favours the supposition of the colouring matter being decomposed. Other interesting theories might be advanced from phenomena observed during the process of croft bleaching; and also the part that boiling in alkali and the sours take in the operation.

The modern process of bleaching, and that which is now almost universally practised, is by means of chlorine. This substance, as has been mentioned (page 59), was discovered by Scheele, who also described its peculiar property of destroying vegetable colouring matters; but M. Berthollet was the first who called the attention of the public to its value as a bleaching agent, in 1785. About the time this chemist was prosecuting his inquiries into the nature of this substance, he was visited by the celebrated James Watt, to whom Berthollet related the results of his experiments upon bleaching, and from this circumstance the inventor of the modern steam-engine became also the introducer of the new process of bleaching into this country.*

The introduction of chlorine, as a bleaching agent, like all other discoveries which tend to overturn old practices, met with a host of opposition. The most prominent objections offered were, that it destroyed the cloth, did not give a permanent white, and that it killed the men who wrought with it. These statements were not altogether groundless, but the force with which they were urged hastened improvements, and effected remedies. The first method of using chlorine was by saturating cold water with the gas, the water taking

* Some give this honour to Professor Copland of Aberdeen; but, from the evidence we have seen, it belongs to Watt, although the difference of time was little.

up about twice its volume of it. The goods were put into this water, after which it was heated to drive off the chlorine, or set it free, that it might act upon the colouring matter; but, the goods being impaired by this process, even when the greatest care was taken, suggested the diluting of the chlorine water; which diluted liquor was found to bleach equally well, and the goods were preserved. The defect of the goods becoming yellow after a few days, suggested alternate boiling with alkaline leys; and the difficulty arising from the workmen being unable to endure the effects of the escaping gas, led to the discovery that alkalies not only absorb a greater quantity of chlorine than water, but that they hold it with greater affinity, not allowing the gas to escape and affect the atmosphere, at the same time parting with it more regularly and effectively to the goods. The alkalies used were soda and potash, and each bleaching-work had its regular apparatus of retorts and carboys, or wooden chests, for the purpose of making their own chloride of potash or soda. This practice is still continued in many print-works, both in Scotland and England, for particular fabrics, or delicate operations, as it is considered much safer and better adapted for certain purposes than the common bleaching powder. In the year 1798, Mr. Tennant of Glasgow patented a process for using a solution of lime for absorbing the chlorine instead of potash and soda; shortly after, the hydrate of lime (slaked lime) was substituted for lime-water, and this is the preparation now used for bleaching, under the names of bleaching powder and chloride of lime. Other minor improvements have been made regarding the quantity of chlorine absorbed by the lime under certain conditions, which will be noticed afterwards.

Notwithstanding all these discoveries and applications, the real nature of the decolouring agent was still unknown: it was prepared by digesting together a mixture of common salt, peroxide of manganese, and sulphuric acid. A decomposition took place, which was explained as follows:—The sulphuric acid combined with the soda of the salt and set the muriatic acid, which was in union with the soda, at liberty. The oxide of manganese gave off a part of its oxygen which combined with the free muriatic acid, and formed oxygenated muriatic acid, a name which was first applied to this new substance; but after being introduced into the arts, this name was considered

too unwieldy for common use, and was therefore contracted into *oxy-muriatic acid.* It was ultimately contracted, by the workmen, into *oxygen*, and, notwithstanding the discovery of Sir H. Davy, in 1811, that oxy-muriatic acid was not common muriatic acid with more oxygen, but a simple body which he called chlorine, the name oxygen is still given to bleaching powder, and all its preparations. This is a serious evil to the workmen; not practically, but for their own understanding; as it identifies chlorine with oxygen, a substance which effects reactions in the operations of dyeing, quite distinct from that with which it is identified. We still remember the difficulty we were in when hearing that it was the oxygen of the air that supported life, and that it was the same oxygen which turned the green colour of the goods while in the vat, to blue when exposed to the atmosphere, and at the same time, seeing bleaching liquor, which was also termed oxygen, destroying blues, and felt that we could not breathe its gas but with the greatest difficulty. To solve this puzzle, every chemical book we could find was examined for remarks on oxygen; but, to our mortification, not one of these works alluded to its bleaching properties. We doubt not but many others have been in the same dilemma. The following order will show our chemical friends the ridiculous position in which dyers and bleachers place themselves by retaining such names:—

"GLASGOW, ———.

"MESSRS. * * Will please send, at their earliest convenience a cask of their strongest oxygen, containing as near as possible 2 cwt., let it be newly made and dry: the last was damp, so that in a few days it became like as much clay, and lost the most of its strength.—Your attention will oblige yours," &c. &c.

The dyer will do well to turn to the article oxygen, and peruse it, and then the absurdity of the above order will be observed.

We are informed that *chemic* is a common name for bleaching liquor in many print-works; and there are many names for other substances, equally unsuitable. We will give a table of these technical terms with their proper designations in another part of the volume. In the meantime we state that there is no better name for the substance we have been

describing than *bleaching powder*, or, if in solution, *bleaching liquor*.

Bleaching powder is prepared by exposing the hydrate of lime (slaked lime) to an atmosphere of chlorine gas till the lime ceases to absorb the gas. In practice, it is found that when the lime is in combination with an extra equivalent of water, it will absorb much more chlorine than when it has just as much water as slakes it. The chlorine is passed into large vessels or chambers furnished with shelves, upon which the lime is placed. Bleaching powder is white and pulverulent: it has a hot, bitter, and astringent taste, and a peculiar smell. When digested in water, carbonate of lime and some other impurities remain.

Some of the continental chemists first suggested that the chlorine was not merely absorbed and retained by the lime, but that it combined with it, and formed one or more definite compounds. This has led to a great deal of research, but scarcely to any definite conclusions, as there are various compounds of chlorine with oxygen which may be formed during the preparation of bleaching powder, and which possess bleaching properties as well as the chlorine alone. The most general supposition is, that hypochlorite of lime is formed, and that on this salt, and its decomposition, depend the operations of bleaching. This opinion is well-founded, and may be taken as expressing the true composition of bleaching powder, which is therefore to be regarded as a definite salt of lime and hypochlorous acid, with chloride of calcium and hydrate of lime: * thus, $CaOClO + CaCl + CaOHO$.

The best bleaching powder of commerce seldom contains above thirty per cent. of chlorine available in bleaching; but there are few of the substances employed by the dyer or bleacher more liable to change; indeed, from its first formation, there seems to be a constant chemical action going on between the chlorine and the lime; oxygen is disengaged, and chloride of calcium formed, a substance which possesses no bleaching properties. These changes may be much retarded by keeping the powder perfectly dry, or by dissolving

* Whoever is desirous of entering into the merits of the researches made upon the chemical character of bleaching powder, will find a series of valuable papers upon the subject, by BALARD, in the 2d volume of the *General Records of Science*.

it in cold water, and keeping the solution excluded from the air. Chloride of lime (bleaching powder) does not attract moisture from the atmosphere, as is supposed by dyers, but when exposed, it is rapidly changed into chloride of calcium, a substance that is very deliquescent, and allowing that the lime previously contained two atoms of water, these combine with the chloride of calcium, when formed, and place this salt in the best circumstances for attracting more water from the air, thus hastening the destruction of the remaining chloride of lime. We have seen good bleaching powder by a little inattention reduced to this state in a few weeks, and its bleaching properties almost totally destroyed.

As chloride of lime loses its bleaching properties by standing and several other circumstances, it is of the utmost consequence to the consumer that he should have some means of determining its real value, both for the sake of safety and accuracy in his processes, and its commercial worth. We have seen bleaching powder, which did not contain above ten per cent. of chlorine, charged and paid for at the same rate as that which contained thirty per cent.; but not having the means of testing it previously, the quality was not discovered till the salt was in solution; indeed, we are not aware of any relative prices according to the quality of this article, although with a very little care and trifling expense the dyer may know the value of the article he is about to purchase, and of course only pay accordingly. The first method of determining the value of bleaching powder was by sulphate of indigo, but the indigo solution alters by keeping, and is therefore objectionable. "Several exact methods," says Graham in his *Elements of Chemistry*, "of which that in which sulphate of iron is used, appears to be entitled to preference. This method is based upon the circumstance that the chlorine of chloride of lime converts a salt of the protoxide into a salt of the peroxide of iron. It is found by experience that ten grains of chlorine are capable of peroxidizing 78 grains of crystallized sulphate of iron. In an experiment to determine the per centage of chlorine in a sample of bleaching powder, some good crystals of protosulphate of iron (copperas) are to be pounded and dried by pressing between folds of cloth; 78 grains are dissolved in about two ounces of water acidulated by a few drops either of sulphuric or muriatic

acid; then 50 grains of the chloride of lime to be examined, are dissolved in about two ounces of water, by rubbing them together in a mortar, and the whole poured into a vessel graduated into a hundred parts. The common alkalimeter will do. This is a straight glass tube, or generally a very narrow jar about $\frac{5}{8}$ths of an inch in width, and 14 inches high, mounted upon a foot, as shown in the accompanying figure, capable at least of containing a thousand grains of water, and graduated into a hundred parts. The jar containing the 50 grains of chloride of lime is filled up to the highest graduation by the addition of water, and the whole is well mixed. The clear part of this solution is gradually poured into the solution of sulphate of iron, till the latter is completely peroxidized. This is known by means of red prussiate of potash, which gives a blue precipitate with the protoxide, but not with the peroxide of iron. A white plate of porcelain or glass is spotted over with small drops of the prussiate; a drop of iron solution is mixed with one of these after every addition of chloride of lime; and the additions continued so long as the prussiate drops are coloured blue. They may be coloured green, but that is of no moment. When the iron is peroxidized, the number of graduations or measures of chloride of lime required to produce that effect is noted; the quantity of chlorine in the 50 grains of bleaching powder is now known, being ascertained by proportion. Thus, if it required 68 measures of the bleaching solution, then, as 68 is to 10, so 100 is to 14·7 the chlorine in the fifty grains of powder; this being multiplied by two gives the per centage of chlorine in the sample, which is 29·4." We have found, in operating in this way, a liability to lose a little chlorine as gas. This is obviated by having the iron solution in a stoppered bottle, and upon every addition of bleaching liquor to put in the stopper and shake the bottle.

Another process has been recommended by Gay Lussac, which combines simplicity with accuracy, and is coming into general use with the manufacturers of bleaching powder. A solution of arsenious acid is made in muriatic acid, and diluted with water. On adding a solution of chloride of lime,

the muriatic acid takes the lime; the chlorine decomposes the water, combining with its hydrogen, while the oxygen unites with the arsenious acid, and converts it into arsenic acid. When the arsenious solution is tinged with sulphate of indigo, and bleaching liquor added, there is no change takes place on the indigo until the whole arsenious acid is transformed into arsenic acid; but the first drop after this discolours the indigo. The correctness of this test is founded upon the knowledge of what proportion of chlorine is necessary to oxidize the arsenious acid in the test solution. Various proportions have been proposed as the standard strength of the solution, but it does not matter much what proportions are used provided the operator knows what proportion of chlorine is necessary to transform it, and being careful always to have it the same. The best proportions for general use are those that require the least calculation. The following proportions we have found to do very well, and to be easily counted. Take one ounce of arsenious acid (common arsenic of the shops), and dissolve it by digestion for a few minutes at a boiling heat, in 24 ounces by measure of pure muriatic acid, then add 46 ounces by measure of distilled water; but in case of any loss by evaporation during digestion, it is better to have a vessel which contains up to a certain mark 70 ounces, and when the acid solution is put into it, to fill up to the mark with water. This may be bottled and put past as the standard test liquor. Every three ounces by measure of it are equivalent to twenty-five grains of chlorine. When a sample of bleaching powder is to be tried, two hundred grains are carefully weighed and dissolved in the manner already described, in twice as much water as will fill the alkalimeter, or any other vessel graduated into a hundred parts. Three ounces of the arsenious solution are measured out and put into a glass jar or tumbler, and tinged with sulphate of indigo. The alkalimeter is now filled with the bleaching liquor, which is added slowly to the arsenious solution, stirring constantly, and watching every drop that is added for the decolouring of the indigo. If the sample be so poor in chlorine that one measure of the alkalimeter will not change the colour of the indigo, it may be filled again, and the process continued till the indigo is decoloured, and the whole number of graduations taken to effect this carefully noted; the fewer the number of graduations required, the richer the sample is in chlorine. Now, as every three

ounces of the test liquor contain arsenious acid equivalent to 25 grains of chlorine, if the hundred measures effect the change of the arsenious into the arsenic acid, the value of the sample is exactly 25 per cent.; in other words, every four graduations taken to effect this change indicate one per cent. of chlorine. These equivalents were practically determined, and may differ a little from the theoretical calculation by atomic numbers, but the difference does not vary above half a per cent., and is not of much consequence in practice. The following table will serve as a guide to those who may adopt our proportions: —

Measures.	Per cent.	Measures.	Per cent.	Measures.	Per cent.	Measures.	Per cent.
150	16·66	127	19·68	104	24·03	81	30·86
149	16·77	126	19·84	103	24·27	80	31·24
148	16·89	125	20·00	102	24·51	79	31·64
147	17·00	124	20·16	101	24·75	78	32·05
146	17·12	123	20·32	100	25·00	77	32·46
145	17·24	122	20·49	99	25·25	76	32·89
144	17·36	121	20·66	98	25·40	75	33·33
143	17·48	120	20·83	97	25·77	74	33·78
142	17·60	119	21·00	96	26·04	73	34·24
141	17·73	118	21·18	95	26·31	72	34·72
140	17·85	117	21·36	94	26·58	71	35·21
139	17·98	116	21·55	93	26·87	70	35·71
138	18·11	115	21·73	92	27·17	69	36·23
137	18·25	114	21·93	91	27·48	68	36·75
136	18·38	113	22·12	90	27·77	67	37·31
135	18·51	112	22·32	89	28·08	66	37·87
134	18·65	111	22·52	88	28·40	65	38·46
133	18·79	110	22·72	87	28·73	64	39·09
132	18·94	109	22·93	86	29·06	63	39·68
131	19·08	108	23·14	85	29·41	62	40·32
130	19·23	107	23·36	84	29·76	61	40·98
129	19·38	106	23·58	83	30·12	60	41·26
128	19·53	105	23·81	82	30·48		

The above table includes almost the whole range of per centage of the bleaching powder of commerce; but should the dyer meet with any not included in the table, the per centage may be calculated as follows. As the number of measures is

to 100, so is 25 to the answer required. Say, for example, the measure is 160,—then 160 : 100 : : 25 : 15·62.

Any of the two methods just described may be performed in a few minutes; and in a substance that is liable to such deterioration, it is surely of importance that the purchaser should have some knowledge of the quality of the article he is purchasing, and that the workmen know something of the strength of the substance they are working with. Might not a certain price be fixed for a standard strength of bleaching powder, and to rise and fall according to the per centage of chlorine which it contains, in the same manner as practised with soda ash? It would at least save much annoyance, and the common complaint, "that the last cask was not so good as the former." The average per centage of good bleaching powder varies from 25 to 30 per cent. Were this average fixed at threepence per pound, which has been the constant price of bleaching powder these some years, then that which contains from 20 to 25 per cent. would be 2½d., and from 15 to 20, 2d. per pound, while above 30 per cent. the value ought of course to rise in the same ratio. The adoption of some such plan, we are confident, would be satisfactory to all parties.

To prepare chloride of lime for bleaching, an aqueous solution is requisite For this purpose a quantity is put into a large vessel filled with water, well stirred, and allowed to settle; this is termed the stock liquor. There are no definite proportions for making up this vat: every bleacher makes up his stock-vat to a certain strength indicated by Twaddell's hydrometer, a most fallacious test, as the chloride of calcium, and every other matter which is soluble in water, although it has no bleaching properties, affects the hydrometer. Care should be taken that this stock-vat be protected from the air as much as possible, as the lime absorbs carbonic acid, and the chlorine being set at liberty, occasions considerable loss. This may be illustrated by putting a little of the solution upon a flat plate, and allowing it to stand a few days, when it will be found to have lost its bleaching power altogether.

The first operation in bleaching cloth is steeping it in a waste ley, or tepid water, for a number of hours, generally over night: this is termed the *rot* steep: its object is to loosen the paste and dirt that may have adhered to the cloth

during its manufacture. This steep ought not to be hotter than blood heat, otherwise, if oil be upon the cloth, it is not saponified, neither is it so easily taken out after; in all cases when oil is observed, it ought to be taken out by rubbing it with soft soap and cold water previous to putting it into the steep. The goods are thoroughly washed from this steep in the dash wheel, but if a wheel is not convenient, they are tramped in water, and then washed by rinsing them through water with the hands; they are then ready for the boiler. The boiling ley is made up by taking strong caustic ley (see soda and potash), a quantity equal to about six pounds weight of alkali to one hundred pounds weight of cloth, having as much water in the boiler as will allow the goods sufficient play when boiling; they ought to boil for three hours. When goods are for light delicate colours, such as Prussian blues, the success of a bleach for such colours depends much upon a good boil. The goods are well washed from the boil, and allowed to drain; the draining is facilitated by pouring hot water upon them; they are then hanked up, taking out all the twists, and laid into the bleaching liquor as loose as possible. The vessels which contain this liquor are large, made either of stone or wood, and are termed bleaching vats, or troughs. To prepare this liquor, these troughs are filled with water, and a quantity of the stock liquor added until the required strength is obtained, which is indicated by its action upon the sulphate of indigo, in what is termed the test-glass, a vessel of this form. It is filled to the mark *a* with the sulphate of indigo, this indigo is generally supplied by the manufacturers of the powder as test blue, the liquor is added drop by drop until the colour of the indigo is destroyed; the quantity taken to effect this is denoted by the graduations above; the weaker the liquor, the greater the number of graduations required; each of these graduations is termed its degree, two degrees are considered a fair strength for light goods, but for heavy fabrics it may be made stronger; they are allowed to steep in this for several hours, varying according to the nature of the goods. The objections we had to the use of sulphate of indigo as a test in the former case are equally applicable here. We have found

this test to be very uncertain. A much better method has been adopted by Mr. Walter Crum, a description of which was read by him to the Glasgow Philosophical Society, and published in the Report of that Society for 1841. We quote the following important paragraphs of the paper :—

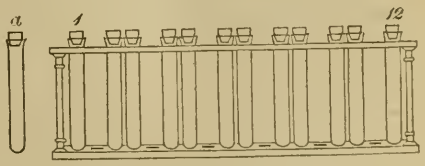
"Chlorimetry requires to be practised by the bleacher for two purposes—First, he has to learn the commercial value of the bleaching powder which he purchases; and with that view he can scarcely desire any thing better than the method either by arsenious acid, or green copperas. But the more important, because the hourly testing of his bleaching liquor, and that on which the safety of his goods depends, is the ascertaining the strength of the weak solutions in which the goods have to be immersed. If the solution is too strong, the fabric is apt to be injured. If too weak, parts of the goods remain brown, and the operation must be repeated. The range within which cotton is safe in this process is not very wide. A solution standing 1° on Twaddell's hydrometer, (spec. grav. 1.005) is not more than safe for such goods, while that of half a degree is scarcely sufficient for the first operation of stout cloth, unless it is packed more loosely than usual. When the vessel is first set with fresh solution of bleaching powder, there is little difficulty, if the character of the powder be known; but when the goods are retired from the steeping vessels, they leave a portion of bleaching liquor behind, unexhausted, which must be taken into account in restoring the liquor to the requisite strength for the next parcel. The chlorimeter must, therefore, be applied every time that fresh goods are put into the liquid. It must, consequently, be intrusted to persons who may not be expert either in figures or in chemical manipulation. Hence all the processes I have described are too delicate and tedious.

"I introduced another into our establishment some years ago, which has been in regular use ever since, and by which the testing is performed in an instant. It depends on the depth of colour of the peracetate of iron. A solution is formed of proto-chloride of iron, by dissolving cast-iron turnings in muriatic acid of half the usual strength. To ensure perfect saturation, a large excess of iron is kept for some time in contact with the solution at the heat of boiling water. One measure of this solution, at 40° Twaddell, (spec. grav. 1.200) is mixed with one of acetic acid, such as Turnbull and Co.

of Glasgow sell at 8s. a gallon. That forms the proof solution. If mixed with six or eight parts of water it is quite colourless, but chloride of lime occasions with it the production of peracetate of iron, which has a peculiarly intense red colour.

"A set of phials is procured, 12 in number, all of the same diameter. A quantity of the proof solution, equal to $\frac{1}{10}$th of their capacity, is put into each, and then they are filled up with bleaching liquor of various strengths, the first at $\frac{1}{12}$th of a degree of Twaddell, the second, $\frac{2}{12}$ths, the third, $\frac{3}{12}$ths, and so on up to $\frac{12}{12}$ths, or 1 degree. They are then well corked up, and ranged together, two and two, in a piece of wood, in holes drilled to suit them. We have thus a series of phials showing the shades of colour which those various solutions are capable of producing. To ascertain the strength of an unknown and partially exhausted bleaching liquor, the proof solution of iron is put into a phial similar to those in the instrument, up to a certain mark, $\frac{1}{10}$th of the whole. The phial is then filled up with the unknown bleaching liquor, shaken, and placed beside that one in the instrument which most resembles it. The number of that phial is its strength in 12ths of a degree of the hydrometer; and by inspecting the annexed table, we find at once how much of a solution of bleaching powder, which is always kept in stock, at a uniform strength of 6 degrees, is necessary to raise the whole of the liquor in the steeping vessel to the desired strength.

"The instrument is formed of long 2 ounce phials cast in a mould; those of blown glass not being of uniform diameter. The outside, which alone is rough, is polished by grinding, and in this state they can easily be procured at 4s. 6d. a dozen. They are placed two and two, so that the bottle containing the liquid to be examined may be set by the side of any one in the series, and the colour compared by looking through the liquid upon a broad piece of white paper stretched upon a board behind the instrument.*



* The above figure represents the instrument fitted with tubes, which serve equally well.

"To explain the table it is necessary to state that the steeping vessels we employ contain, at the proper height for receiving goods, 1440 gallons, or 288 measures of 5 gallons each,—a measure being the quantity easily carried at a time. In the following table, 0 represents water, and the numbers 1, 2, 3, &c., are the strength of the liquor already in the vessel in 12ths of a degree of Twaddell, as ascertained by the chlorimeter. If the vessel has to be set anew, we see by the first table that 32 measures of liquor at 6° must be added to (256 measures of) water to produce 288 measures of liquor at $\frac{8}{12}$ths of a degree. But if the liquor already in the vessel is found by the chlorimeter to produce a colour equal to the 2d phial, then 24 measures only are necessary, and so on.

To stand $\frac{8}{12}$°		To stand $\frac{6}{12}$°	
0 requires	32 measures.	0 requires	24 measures.
1 —	28 —	1 —	20 —
2 —	24 —	2 —	16 —
3 —	20 —	3 —	12 —
4 —	16 —	4 —	8 —
5 —	12 —	5 —	4 —
6 —	8 —		
7 —	4 —		
To stand $\frac{4}{12}$°		To stand $\frac{3}{12}$°	
0 requires	16 measures.	0 requires	12 measures.
1 —	12 —	1 —	8 —
2 —	8 —	2 —	4 —
3 —	4 —		

"Let us see what takes place on mixing chloride of lime with protomuriate of iron. On the old view of the constitution of bleaching powder—that it is a combination of chlorine and lime, we have—

$$\left.\begin{matrix} 3\ (CaO,\ Cl) \\ 6\ FeCl \end{matrix}\right\} \text{becoming} \left\{\begin{matrix} 3\ CaCl \\ 2\ Fe_2Cl_3 \\ Fe_2O_3 \end{matrix}\right.$$

the peroxide of iron forming peracetate with the acetic acid which is present. Or, supposing with Balard that when two atoms of chlorine unite with two atoms of lime, the product is CaCl + CaO, ClO, we have this formula:

$$\left.\begin{matrix} 3 & CaCl \\ 3 & (CaO,\ ClO) \\ 12 & FeCl \end{matrix}\right\} \text{ becoming } \left\{\begin{matrix} 6 & CaCl \\ 4 & Fe_2Cl_3 \\ 2 & Fe_2O_3 \end{matrix}\right.$$

"Here one third only of the iron goes to form the deep coloured peracetate, while the whole might be employed for that purpose, by using protoacetate instead of protochloride. The latter however is preferred, from the greater tendency of the acetate to attract oxygen from the air, and consequently the greater difficulty of preserving it. Even with the chloride it is best to give out small quantities at a time, preserving the stock in well closed bottles."

From this description it will be seen that the method recommended by Mr. Crum may be adopted for testing the per centage of the powder, as well as the strength of the liquors.

To return to the bleaching process. The goods being allowed to steep in the bleaching liquor for some hours, they are lifted and washed, after which, if they are thick stout goods, they are put into a sour for a little, then washed, and go through the same operations of boiling, liquoring, and souring, as before; but for all common fabrics, we have found it the best practice to *sweeten* * the goods from the liquor, hank them anew, and put them back into a new liquor of the same strength for a few hours, wash them from this, and allow them to steep for an hour in strong sour of vitriol and water, about $1\frac{1}{2}$ pint of the former to four gallons of the latter.

There is perhaps no single branch connected with the art of dyeing upon which there is more difference of opinion than bleaching. Every one has some peculiarity of his own; but, when the peculiarities are all compared, the difference in general is only nominal. One thing may be noticed, namely, the necessity of washing the goods well from the liquor before souring, as any lime remaining upon the cloth will be formed into an insoluble sulphate, and resist the dye. Some main-

* Building the goods on a drainer, and pouring water upon them till the water ceases to taste of liquor as it comes from them is termed *sweetening*.

tain that this is of no consequence; in our opinion, it depends wholly upon the colour which is to be dyed on the cloth. We have found that light pinks, light greens, light lavenders, and sometimes light blues, when not washed well from the liquor, were often full of white spots, which we ascribed to that cause, although there are white spots often occurring both on yarn and cloth from other causes; but, for other dark shades we found no difference, and for colours to be dyed with the bichromate of potash (chrome), such as yellows, ambers, and orange, we seldom gave them any sour, only washed from the first liquor, and then dyed.*

Cotton, in the hank (yarn), when it is to be finished white, goes through the same process as cloth, with the exception of the *rot* steep; but, for dyeing, a quicker operation is adopted. All cotton yarn must be boiled in water for three or four hours previous to being dyed. Every lot of ten pounds weight, constituting what is termed a bundle, is divided into six equal numbers of *spindles*, and hung upon wooden pins about three feet long, and two inches thick; this is termed *sticking*.

The stock-liquor for yarn is generally prepared in a cask containing about 120 gallons of water; to this is added about 20 lbs. of good bleaching powder, stirred, and allowed to settle. A small tub of a size in which a bundle is wrought freely, termed a ten pound tub, is filled nearly two-thirds full with boiling water, and a bucket or *pailful* (about four gallons) of the stock liquor added. The bundle is now let down as quickly as possible, and turned over for about ten minutes, after which it is put through a second tub of the same size, with water made a little sour by adding about an imperial gill of vitriol. It is wrought in this for about five minutes. Being then well washed, it is ready to be dyed of almost any light shade. By this method two men can bleach and wash two hundred pounds weight of yarn in about three hours, a quantity which, by the other process of boiling, steeping, and souring, would have occupied two days.

Having detailed the present method of bleaching cotton goods for dyeing, we may say a little upon the chemical nature of these processes. Previous to the discovery of the

* In souring fine goods the vessel used is of consequence. In using a vessel lined with lead, there was experienced for a long time a constant occurrence of small holes in the goods. On changing the vessel for a wooden one, this evil has entirely disappeared. The cause of the holes has not however, been determined.

elementary nature of chlorine, when that substance was considered a compound of muriatic acid and oxygen, it was thought that the acid parted with its oxygen, and that this constituent bleached the goods in the same way as atmospheric air in croft bleaching, but more rapidly. When the true nature of chlorine was discovered, the theory was somewhat changed; finding, as was then supposed, that chlorine did not bleach except water was present, it was considered that the chlorine united with the hydrogen of the water forming muriatic acid, and that the liberated oxygen was still the bleaching agent.

This theory is still maintained and supported by various analogies. We quote the following from Gregory and Liebig's edition of *Turner's Chemistry:* "One of the most important properties of chlorine is its bleaching power. All animal and vegetable colours are speedily removed by chlorine, and when the colour is once destroyed, it can never be restored. Davy proved that chlorine cannot bleach except water be present; thus dry litmus paper suffers no change in dry chlorine, but when water is admitted, the colour speedily disappears. It is well known also, that hydrochloric acid (muriatic acid) is always generated when chlorine bleaches. From these facts it is inferred that water is decomposed during the process, that its hydrogen unites with chlorine, and that decomposition of the colouring matter is occasioned by the oxygen liberated. The bleaching property of binoxide of hydrogen, and of chromic, and permanganic acids, of which oxygen is certainly the decolouring principle, leaves little doubt of the accuracy of the foregoing explanation."

Another theory has been advanced, and equally if not more tenable, by which the chlorine is supposed to act directly upon the colouring matter. The following is from Sir Robert Kane's Treatise on Chemistry:—"Formerly it was considered that water was necessary for this bleaching, and that the chlorine combined with the hydrogen, while the oxygen of the water being thus thrown upon the organic substance, oxidized it, and formed a new body, which was colourless. I have shown, however, that this is not the case, but that the chlorine enters into the constitution of the new substance formed, sometimes replacing hydrogen, at others, simply combining with the coloured body, and in some, the reaction being so complete, that its immediate stages cannot be completely traced."

This theory is also supported by several analogies, such as the action of chlorine upon indigo already noticed; but which of the changes, alluded to by Sir Robert Kane takes place during the bleaching of cotton, is not yet known. Chloride of lime, says the same author, does not bleach except an acid be present to combine with the lime, and set the chlorine at liberty; but this is only conditional. It is true, that if blue litmus paper be put into a solution of newly dissolved chloride of lime, it is not bleached; but if the solution be allowed to remain in contact with the air for an hour or two, the lime combines with the carbonic acid of the atmosphere; and if the blue litmus paper be put into this solution, it is instantly bleached by the liberated chlorine. Cotton that has not been boiled in alkalis, is acted upon as the litmus paper in both cases; but if the cotton has received a good alkaline boil, and is well washed, the bleaching process goes on, although the bleaching powder be newly dissolved. This shows that the alkaline leys effect a change upon the colouring matter. The nature of this change we are not as yet prepared to state: several opinions have been given, but they are hypothetical, and some of them are not borne out by practice. Neither is the theory of Sir Robert Kane, of the formation during bleaching of a colourless chloride, or oxide, at all admissible, at least as regards cotton. According to this theory, goods being bleached by having formed upon them a new compound would become heavier, whereas practice shows that the operation of bleaching causes the goods to lose about 3 per cent. in weight. From several experiments which we made, we found that the loss by boiling was 5 per cent., and by bleaching 3 per cent., in all 8 per cent.

Whenever the cloth is put into the bleaching liquor, there are acids formed, the principal of which is the hydrochloric; but whether it is from the chlorine combining with the hydrogen of the water, or the colouring matter of the goods, we cannot say, the latter we think most probable. Our opinion is, that the chlorine combines with the hydrogen of the colouring matter; and according to a law we have several times alluded to, the remaining elements of the colouring matter form a new substance, which is soluble, and thus the whole colouring matter is taken off the cloth. In vats, where several hundred pounds weight of cotton have been bleached before changing the liquor, there is evidence of

more substances remaining than merely a solution of muriate of lime; but what these are, we dare not as yet venture to assert.

The effects of light in the operation of bleaching, also favours this hypothesis, for we know that exposure to the sun facilitates the process very much. This circumstance, however, tells in favour of the theory that the oxygen is the bleaching agent, as well as in favour of the theory which makes the chlorine the bleaching agent. There is only this difficulty, which, however, must not be overlooked, namely, that if a solution containing chlorine is exposed to the light, there is a decomposition of the water; for the chlorine combines with the hydrogen, and liberates the oxygen of the aqueous molecule. The oxygen would again, by this theory, require to combine with the hydrogen of the colouring matter, and form water, a series of affinities which we cannot conceive, for if the affinity of the chlorine be stronger for the hydrogen than for the oxygen of the water, it would necessarily take the hydrogen from the colouring matter, seeing that oxygen, which by this showing has the weaker power, decomposes it to form water again, a series of reactions altogether irreconcileable with one another. That the oxygen combines with the colour, forming a colourless oxide, is quite irreconcileable with the practical fact of the goods losing weight by bleaching.

Such is an outline of the processes of bleaching cotton goods for dyeing, as practised in most dyeworks at the present day. Woollen and silk are bleached by exposing them after being boiled or scoured, to the vapour of sulphurous acid, which process will be noticed under sulphur; but they are not thus bleached for dyeing.

Ozone.—Within these few years a substance, or property, which has got the name of Ozone, has been discovered to have extraordinary bleaching properties. If a few sticks of phosphorus be placed in a large bottle containing a little water at bottom, and corked, in a short time the atmosphere of the bottle is found to possess peculiar properties, and is said to contain ozone, and acts in relation to a great many substances the same part as chlorine. Professor C. F. Schönbein, the discoverer of this substance, and who has made it the subject of careful investigation, was able to bleach, or decolour, sulphate of indigo, and also many flowers, by means of it. The real character of ozone is as yet only imperfectly

understood. The discoverer supposes it to be a volatile peroxide of hydrogen; and this idea has been to some extent verified by experiments, while others suppose it to be a new condition of oxygen. However, enough is known of it to induce us to think that when easy methods of producing and applying it are discovered, ozone will be found of much value in the arts.

SULPHUR (S. 16).

Sulphur has been known from the earliest ages. It is found in large quantities, uncombined, in the neighbourhood of volcanoes; and is also extensively diffused through nature in combination, especially with metals. It is obtained in great abundance by roasting the sulphurets of iron, lead, copper, and zinc.

Sulphur is a hard, brittle, substance, of a greenish-yellow colour. It is not soluble in water, and is not changed by exposure to the air. When heated to the temperature of 170° Fah. it sublimes, and deposits again in the fine powder well known as the *flowers of sulphur*. If heated in a close vessel, say a glass flask, to 218° Fah. it melts and becomes liquid as water, but by increasing the heat it undergoes some curious changes; at 340° it begins to get thick, and assumes a reddish colour, and if the heat be continued, it becomes so thick that it will not pour from the vessel. At 482° it begins to become thinnner, and continues thinning until it boils at 750°. When suddenly cooled from its most fluid state, which is about 224°, by throwing it into cold water, it becomes instantly brittle; but if cooled in the same manner, when thick (about 400°), it remains quite soft, and may be drawn into threads. If heated in the open air to about 300° it takes fire, and burns with a pale blue flame, and gives off most suffocating fumes of sulphurous acid gas.

SULPHUR combines with oxygen in several proportions, forming acids of considerable importance in the arts. These are:—

Sulphurous acid.....SO_2
Sulphuric acid.....SO_3 Anhydrous
Hyposulphurous acid.....S_2O_2
Hyposulphuric acid.....S_2O_5

Sulphurous Acid is a gaseous substance, and is always pro-

duced when sulphur is burned in the air, or in oxygen. It may be prepared also from the compounds of sulphur. If sulphuric acid be heated in contact with metallic copper, or charcoal, sulphurous acid is given off. We have:—

$$2\ SO_4\ H \text{ and } Cu = SO_4\ Cu\ SO_2 + 2\ HO$$

If charcoal be used instead of copper in this experiment, carbonic gas is also liberated. It may also be prepared by heating together 3 parts flowers of sulphur, and 4 parts black oxide of manganese, in a similar apparatus to that described for the preparation of oxygen from manganese.

This gaseous acid, as has been stated, is much used in bleaching animal substances, as silk and woollen; and also some vegetable substances, as straw. For these operations the gas is procured by merely burning the sulphur in the air. The articles to be bleached are put into a chamber, or box, made as tight as possible, in which is placed a small pan of sulphur, which is kindled by putting into it a piece of red hot iron. The chamber is then closed, and the articles, damp and well spread out, are thus exposed to the sulphurous fumes. The gas is absorbed in the first place, by the water on the goods, and is thus brought into immediate contact, and enabled to combine with the fabric. Goods bleached by this gas are increased in weight, showing a combination; they are not permanently white, showing that the compound formed is decomposed, indeed, the gas gradually escapes, and by immersing the goods in a stronger acid, the white compound is decomposed. This may be beautifully illustrated by exposing a red rose to the fumes of sulphurous acid gas, it is bleached white, but by putting it into a *sour* (vitriol and water), the red colour is restored. This shows the distinctive characters of this gas and chlorine, as bleaching agents, and that any analogy drawn between them to support a theory is groundless. Some bleachers of woollen pass the goods through a solution of sulphurous acid in water, instead of *stoving* them. Bleaching by this gas is not done with goods that are to be dyed.

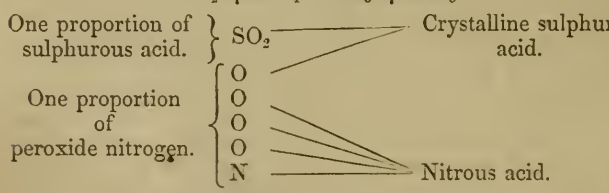
Sulphurous acid passes readily into sulphuric acid by absorbing more oxygen. In newly distilled water, or water having no air or oxygen dissolved in it, sulphurous gas may be kept a long time if well corked up, but without these precautions it very soon combines with the oxygen dissolved

in the water. If a quantity of peroxide of iron is put into a solution of this gas, it passes into the state of sulphuric acid, and protoxide of iron. The formula is

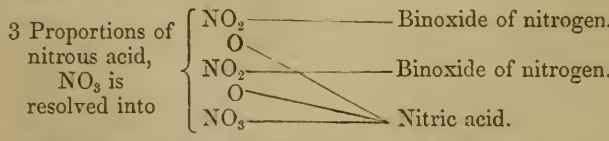
$$Fe_2\,O_3 + SO_2 = SO_4\,Fe + FeO$$

Sulphuric Acid is one of the most important of the compounds of sulphur; it is not produced by the direct action of its elements, but generally from the oxidation of sulphurous acid. We mentioned when treating of nitrogen, (page 50) that the binoxide of nitrogen on coming into contact with the air combines with more oxygen, and is converted into the peroxide of nitrogen; and that this compound readily yields its oxygen again to other bodies which have a strong attraction for it. If sulphurous acid is brought into contact with peroxide of nitrogen in the presence of water, a decomposition takes place, and there is formed sulphuric acid and nitrous acid, which may be represented by the formula,

$$SO_2 + NO_4 = SO_3 + NO_3$$



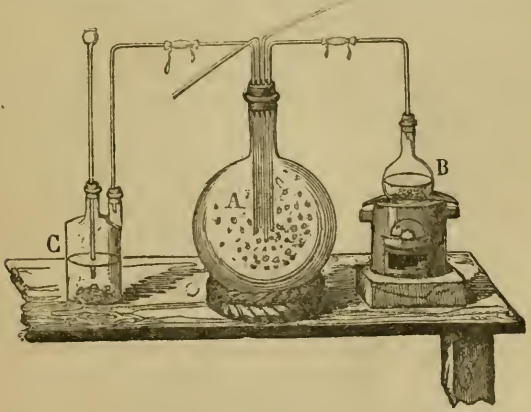
Both of these compounds when formed are taken up by the water, the first forming hydrous sulphuric acid, the second is decomposed, every three proportions being resolved into $3\,NO_2 = 2\,NO_2 + NO_5$



The nitric acid remains in the water with the vitriol, but the binoxide of nitrogen rises to the surface and imbibes oxygen, and is again converted into peroxide, ready to undergo again the same changes. On the large scale these changes and reactions are brought about by causing the sulphurous acid fumes from burning sulphur, and the peroxide of nitrogen

fumes from pouring sulphuric acid upon nitrate of soda or potash, to pass together into large leaden chambers along with a jet of steam. In this chamber the reactions above described go on. At the bottom of this chamber is a layer of water for absorbing the acids formed; and at the top is an aperture to admit air, so that the binoxide of nitrogen becomes peroxidised as it rises to the top. The water from the bottom is drawn off at short intervals as it becomes impregnated with the acid. These intervals are so arranged that the specific gravity of the acid when drawn off is about 1·600 = 120° Twaddell. It is then evaporated in leaden tanks, until the specific gravity becomes about 1·76, or 152° Twaddell. If the operation were continued further, the acid would act upon the lead; it is consequently transferred to vessels of glass or platinum, and evaporated until the specific gravity rises to about 1·847, or 169⅛ Twaddell.

The whole of the operation of making sulphuric acid may be done, for illustration, by the following simple apparatus:—



Generate sulphurous acid SO_2 in one bottle, (B) and peroxide of nitrogen NO_4 in another (C), and cause the two gases to meet in a third bottle (A), having a little water at bottom; the formation of sulphuric acid will go on as described, and be found in the water of the condensing vessel (A) after the operation.

A great quantity of sulphuric acid is made by burning iron pyrites, a native compound of iron and sulphur. This mineral often contains arsenic, which the sulphurous acid carries with it into the acid-chamber; and therefore the vitriol made from this source, contains arsenic as an impurity.

Sulphuric acid may also be prepared by putting a quantity of sulphate of iron into an earthenware retort, and applying a strong heat to it; the sulphuric acid is distilled over, and peroxide of iron remains. This is the oldest method of obtaining sulphuric acid and is still practised in some parts of Germany. The acid so obtained is very strong; has a dark colour, and gives off a quantity of white fumes; hence it is called *fuming sulphuric acid.* It is also called Nordhausen acid, from its being manufactured there. When this acid is poured into cold water, it produces a hissing noise, like that produced by putting a red hot iron into water. This acid is excellently adapted for making sulphate of indigo.

Sulphuric acid may be mixed with water in any proportion, but there seems to be certain definite quantities with which it will combine with water chemically. When added to water, there is always heat evolved; this heat is a definite quantity, and accompanied by a condensation of bulk, as the dyer may easily convince himself by taking measured quantities of strong vitriol and water, and mixing them; when the mixture is cool, he will find a considerable diminution of bulk. The following experiments upon the amount of condensation, and heat given out, were performed with a common alkalimeter and thermometer.

Measure of Water.	Measure of Acid.	Heat when mixed.	Increase of heat.	Loss by condensation.
90	10	86°	40°	5
80	20	116°	70°	7
70	30	154°	108°	8
60	40	188°	142°	9½
50	50	210°	164°	11
40	60	212°	166°	11
30	70	200°	154°	9
20	80	164°	118°	8½
10	90	136°	90°	7

The above is the mean of three trials. The proportions

of acid and water were taken to make 100 graduations, and mixed. The heat was observed immediately after mixing, and the mixture was kept in a stoppered bottle until cold, when it was measured by the alkalimeter, and the loss by condensation noted. The heat of the water and acid separately, was 46°. The acid used was specific gravity 1·795, taken by Twaddell, 179°. Another proof that water and sulphuric acid form a definite compound is, that when the acid has the specific gravity of 1·78, the composition is $SO_4H + HO$. This, at a temperature of 32° will crystallise in large and regular crystals, while stronger, or weaker acid, at the same temperature will not crystallise. This is a circumstance sometimes experienced in the dyehouse, and is commonly taken as an evidence of impurity in the acid, which, however, it is not.

The ordinary impurities in sulphuric acid are lead, nitric acid, arsenic, and sometimes sulphate of potash which is added to give it density. The presence of lead is easily detected by diluting a little of the acid with distilled water; sulphate of lead is not soluble in dilute acid, and when present, there is produced a milkiness in the solution, as is often seen in the dyehouse when the acid is added to water. Nitric acid may be detected, as described page 57, by suspending a clean crystal of sulphate of iron in the acid, and heating it, a black ring is then seen, or the smell of peroxide of nitrogen perceived. Sometimes a little of this peroxide is present in the acid, and either of these impurities is very bad when the sulphuric acid is to be used for indigo, garancine, or any organic substance. Arsenic may be detected by diluting the acid, and passing a current of sulphuretted hydrogen through it, which gives a yellow precipitate when arsenic is present. This substance, however, is not deleterious in those operations of the dyehouse wherein sulphuric acid is used. Sulphate of potash, or soda, may be detected by putting a few drops of acid into a small basin, and saturating it with ammonia, then evaporating to dryness, and continuing a strong heat until all white fumes of sulphate of ammonia cease; nothing will remain if the acid is pure.

After ascertaining that the acid is pure, the hydrometer may be used to discover its strength. The following table will be useful in this operation:—

Liquid acid.	Specific gravity.	Dry acid SO_3 in 100 parts.	Liquid acid.	Specific gravity.	Dry acid SO_3 in 100 parts.
100	1·8485	81·54	50	1·3884	40·77
99	1·8475	80·72	49	1·3788	39·95
98	1·8460	79·90	48	1·3697	39·14
97	1·8430	79 09	47	1·3612	38·32
96	1·8400	78·28	46	1·3530	37·51
95	1·8376	77·46	45	1·3440	36·59
94	1·8336	76·65	44	1·3345	35 88
93	1·8290	75 83	43	1·3255	35·06
92	1·8233	75·02	42	1·3165	34·25
91	1·8179	74·20	41	1·3080	33·43
90	1·8115	73·39	40	1·2999	32·61
89	1·8043	72·57	39	1·2913	31·80
88	1·7962	71·75	38	1 2826	30·98
87	1·7850	70·94	37	1·2740	30·17
86	1·7774	70·12	36	1·2654	29·35
85	1·7673	69·31	35	1·2572	28·54
84	1·7570	68·49	34	1·2490	27·72
83	1·7465	67·68	33	1·2409	26·91
82	1·7300	66·86	32	1·2334	26·09
81	1·7245	66·05	31	1·2260	25·28
80	1·7120	65·23	30	1·2184	24·46
79	1·6993	64·42	29	1·2108	23·65
78	1·6870	63·62	28	1·2030	22·83
77	1·6750	62·78	27	1·1956	22·01
76	1·6630	61·97	26	1·1876	21·20
75	1·6520	61·15	25	1·1792	20·38
74	1·6415	60·34	24	1·1706	19·57
73	1·6321	59·52	23	1·1626	18·75
72	1·6204	58·71	22	1·1549	17·94
71	1·6090	57·89	21	1·1480	17·12
70	1·5975	57·08	20	1·1410	16·31
69	1·5868	56·26	19	1·1330	15·49
68	1·5760	55·45	18	1·1246	14·68
67	1·5648	54·63	17	1·1165	13·86
66	1·5503	53·82	16	1·1090	13·05
65	1·5390	53·00	15	1·1019	12·23
64	1·5280	52·18	14	1·0953	11·41
63	1·5170	51·87	13	1 0887	10·60
62	1·5066	50·55	12	1·0809	9·78
61	1·4960	49·74	11	1.0743	8·97
60	1·4860	48·92	10	1·0682	8·15
59	1·4760	48·11	9	1·0614	7·34
58	1·4660	47·29	8	1·0544	6·52
57	1·4560	46·48	7	1·0477	5·71
56	1·4460	45·66	6	1·0405	4·89
55	1·4360	44·85	5	1·0336	4·08
54	1·4265	44·03	4	1·0268	3·26
53	1·4170	43·22	3	1·0206	2·45
52	1·4073	42·40	2	1·0140	1·63
51	1·3977	41·58	1	1·0074	0·82

The presence of sulphuric acid is detected by adding to any compound in solution a salt of barium, which gives a white precipitate not soluble in nitric acid. Sulphuric acid has a strong attraction for water, so much so, that if left exposed to the atmosphere, it will absorb moisture and become dilute. A saucer half filled with strong sulphuric acid will become full in a few days by exposure to the atmosphere of a dye-house. This shows the evil of leaving the stoppers out of the bottles, or as is often the case, leaving quantities of this acid in an open jug. Animal and vegetable substances put into sulphuric acid become charred; the hydrogen and oxygen of these bodies go to form water, which combines with the acid, and the carbon is left as charcoal; this is the effect it produces upon the skin. The presence of these matters also tends to weaken the acid, and should therefore be avoided as much as possible. This may be the proper place to refer to a bad practice we have seen in the dye-house. When using vitriol, the jug containing it is often placed upon the floor for convenience, and a workman passing that way comes against it with his foot, and not only spills the acid, but occasionally his shoe is filled with it. When this happens, the first impulse, which is often obeyed, is to plunge the foot into water, when, of course, the mixture of vitriol and water in the shoe is brought nearly to the boiling point, as may be learned from the table above. Severe accidents by this reckless habit are not uncommon. When such an accident does take place, the person ought to take off his shoe and stocking before putting his foot in water; and if his foot has been previously dry, or merely moist, he will escape unhurt. The hand, if dry, may be kept in strong vitriol for some time without burning, but very shortly the acid begins to decompose the skin, and then pain is felt.

Hyposulphurous Acid.—This acid is of singular composition; although it is composed of equal equivalents of sulphur and oxygen, what might be termed SO, yet it is represented double $S_2 O_2$. This seeming anomaly is got over by supposing it to be a compound of sulphurous acid with sulphur, thus: SO_2+S. This acid is not prepared directly from its elements, but is formed either in combination as a salt, or by double decomposition. If a current of sulphurous acid gas SO_2, and sulphuretted hydrogen gas SH, are passed through water

together, four parts or equivalents of the former, and two parts or equivalents of the latter, combine to form three equivalents of hyposulphurous acid, and two of water. The formula may be accordingly this:—$4SO_2$ and $2SH = 3SO_2S$ 2HO. The acid when uncombined is very unstable; after exposure for a short time it deposits sulphur, and sulphurous acid remains.

When a solution of soda or potash is boiled with sulphur, there is formed in the liquid hyposulphate, and sulphuret, of the base, supposing that soda is employed, then four proportions of sulphur, and three of soda, produce

One hyposulphite of soda $NaO\ S_2O_2$ and
Two sulphuret of sodium 2NaS.

The hyposulphites are not yet much used in dyeing; but from the property which the alkaline salts of this acid has of dissolving many metallic oxides, it might undoubtedly be advantageously applied for several purposes.

Hyposulphuric Acid.—This acid is easily formed in combination by passing a current of sulphurous acid through water in which is diffused a quantity of black oxide of manganese; two proportions of the acid combine with one proportion of oxygen from the manganese, and form the hyposulphuric acid, which combines with the remaining manganese to form the hyposulphate of manganese:—

$$MnO_2\ 2SO_2 = MnO\ S_2O_5.$$

This acid may be obtained free from the manganese by precipitating that metal, but cannot be freed from water. Its hydrate is moreover very unstable, but in union with bases it forms salts of great stability.

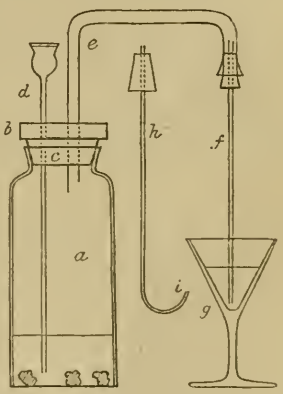
Sulphuretted Hydrogen.—Sulphur combines with hydrogen in equal equivalents, and forms a gaseous compound very useful as a test—this is sulphuretted hydrogen, or sulphide of hydrogen, which is not inappropriately termed hydrosulphuric acid, as the gas has acid properties. This gas is prepared by acting upon a metallic sulphuret, with an acid in this manner:—a few pieces of proto-sulphuret of iron are put into a glass or porcelain vessel containing a little water, and a small quantity of sulphuric or hydrochloric acid is added; a gas of a strong, suffocating smell immediately begins to come off, which

is sulphuretted hydrogen. The reaction which takes place is as follows:—

Sulphuret of iron, $\begin{cases} S \\ Fe \end{cases}$ — Sulphide of hydrogen.

Sulphuric acid, $\begin{cases} H \\ SO_4 \end{cases}$ — Sulphate of Iron.

This gas is absorbed by water, and is sometimes used in solution as a test. It is also taken up in great quantity by a solution of ammonia, forming hydrosulphuret of ammonia, also much used as a test. When used for this purpose in the gaseous state, such an apparatus as the accompanying will serve. The sulphuret of iron, or other sulphuret, is put into the bottle *a*, containing some water, and the acid is added by the long funnel *d*. The gas escapes by the tube *e*, *f*, and passes through the solution to be tested, contained in the glass *g*. The same apparatus serves for passing the gas through water or liquid ammonia, when it is required to produce a saturated solution. The precipitates formed by passing this gas through solutions of various substances, are very characteristic. Thus, a solution containing—



Antimony produces .....Orange precipitate.
Tin and Arsenic .....Yellow precipitate.
Manganese ....Flesh red precipitate.
Zinc.....White precipitate.
Lead, Copper, Iron, &c.....Black precipitate.

Sometimes, however, it is necessary to add a little ammonia before these results are obtained.

Sulphuretted hydrogen is evolved from decaying animal and vegetable matters, and from dunghills, common sewers, and putrifying bodies that contain sulphur. It is very deleterious

to health, and care should be taken to avoid breathing it. The effect of this gas upon many dyes is so very great, that the slightest quantity in the atmosphere is hurtful. It gives to chrome yellows and oranges, a smoky appearance, which cannot be removed; and to spirit reds, it gives a rusty brown appearance. Wherever, indeed, there is a metal present in the dye, this gas affects the colour. Sulphur does so also, consequently the same effects are often produced by burning sulphury coals in a drying stove. We have seen a whole stove-charge of goods, yarn and cloth, spoiled in this way; the colours appearing as if dried in smoke, and the watchman superintending the stove, notwithstanding his protestations that there was no smoke, compelled to bear the blame of negligence.

Sulphur combines with hydrogen in another proportion, and forms a bisulphuret HS_2, which is an oily liquid of no known importance in any process of the dyehouse.

Selenium (Se 39·5).

This element very much resembles sulphur in its properties, and in some of its combinations. It is solid, of a dark brown colour and metallic lustre; and is found in nature in combination with some of the metallic sulphurets, as those of copper, silver, lead, &c. It is very rare, and as it has only been obtained in minute quantities, it has not yet been introduced into the arts, or applied to any useful purpose.

Phosphorus (P 32).

Phosphorus is a soft, solid substance, of a light amber colour, and insoluble in water. It is very abundant in nature in combination with other substances, but principally with lime in the bones of animals. It is exceedingly inflammable, oxidates rapidly when exposed to the air, and emits light visible in the dark, from which circumstance it derives its name. It is manufactured from the bones of animals, by various complicated methods not very easily imitated on a small scale.

This element unites with oxygen in various proportions,

and most of the compounds formed have acid properties, as :—

Suboxide of phosphorus,...P_2O.
Hypophosphorous acid,.....PO.
Phosphorous acid, ...PO_2.
Phosphoric acid, ...PO_5.

These acids all unite with bases, forming salts which are interesting in their relations to each other, and also to salts of other acids. Phosphoric acid and the phosphates, evince peculiar properties in combining with various proportions of water, and producing compounds which differ characteristically from one another. These combinations have been extensively investigated by Professor Graham and other chemists. We are not aware that any of these salts are used in the operations of dyeing, except in so far as they constitute a portion of the salts in dung, and the substance called *dung substitute*, used in dyeing turkey reds and other madder colours.

Phosphorus combines also with hydrogen, nitrogen, chlorine, and sulphur, and likewise with many of the metallic elements forming the class of compounds termed *phosphurets*, or phosphides.

Iodine (I 127·1).

Iodine is obtained from the ashes of sea weed. The ashes are put into water, and the soluble portions are withdrawn, and boiled down. During the process common salt and other salts are deposited and withdrawn; and when the liquid is reduced to a very small quantity and attains a dark colour, a little sulphuric acid is added; the whole is then allowed to remain at rest for a day or two. The liquor is then mixed up with oxide of manganese, and put into a retort, to which heat is applied. The iodine distils over, and is condensed in receivers fitted to the retort.

Iodine is a solid substance, of a metallic lustre, and a bluish black colour; it stains the hands yellow if touched, and is volatile at a low heat, rising in vapour of a beautiful violet colour. It combines with nearly all the non-metallic elements, and also with the metals; with many of the latter it forms compounds having beautiful colours, suitable in every way as

dyes. But from the volatile nature of iodine, the colours produced by it are fugitive, and do not bear exposure. Many attempts have been made to employ the salts of iodine as dye-drugs, and to fix the colour, but they have all failed.

The compounds of iodine with oxygen, are the two acids:

Iodic acid.....IO_5. | Hyperiodic acid.....IO_7.

These acids combine with bases to form salts termed iodates. It forms an acid with hydrogen, namely:—

Hydriodic acid,.....HI.

The salts which this acid forms are termed hydriodates.

Iodine combines with starch, and forms a deep blue violet colour, which soon passes away. The principal compound with which experiments upon the colours formed by iodine may be carried on, is the iodide of potassium, KI. This is easily prepared by boiling iodine in a solution of caustic potash to dryness, then fusing the dry mass in an iron vessel or crucible. The result of this is iodide of potassium, which is easily soluble in water. This salt is abundant, and always very pure in commerce. A little of the solution added to a salt of lead produces a beautiful yellow precipitate, which when boiled in water, and the clear part set aside to cool, gives brilliant golden-coloured crystals in scales. The salts of mercury give with iodide of potassium a deep orange red precipitate. This salt indeed gives precipitates and colours with the salts of nearly all the metals; and, were it possible to render the colours it affords permanent, it would no doubt become a most useful drug in the hands of the operative dyer.

Bromine (Br 80).

Bromine is another element obtained from the ashes of certain sea-weeds, but not in nearly so great abundance as iodine. It is a liquid at ordinary temperatures; has a deep red colour, and is much heavier than water, in which it is generally kept to prevent it volatilizing as it does rapidly when exposed to the air. It has a very penetrating odour, and its fumes destroy vegetable colouring matters, leaving merely a yellow tint.

Bromine is known to combine with oxygen in only one

proportion = BrO_5. This is bromic acid, which combines with bases, forming the salts termed bromates. With hydrogen it combines and forms hydrobromic acid = HBr, the salts of which are termed hydrobromates. It also unites directly with some of the other elements forming bromides, of which the bromide of potassium is an example. The compounds of bromine with some of the metals might also form a dye were they procured abundantly; but the same objection to iodine is also applicable to bromine, it is unstable, and vanishes on exposure.

Bromine and some of its compounds have been much used in the operations of daguerreotyping.

Fluorine (Fl 18·9).

This element is only known in combination, and has never been obtained free. By its powerful attraction for every other substance, it fulfils in some degree the old hypothetical notion of a universal solvent. It is however very abundant in nature, combined with calcium as a fluoride, forming the mineral *fluor spar*. It is not known to combine with oxygen, but it combines very readily with hydrogen, and forms hydrofluoric acid = HFl. This acid may be evolved from fluor spar by acting upon it with sulphuric acid. It dissolves glass, and all matters containing silica, and therefore cannot be kept in glass, china, or earthenware vessels; and as it dissolves all metals except lead, silver, gold, and platinum, it can only be kept in vessels made of any of these metals, but lead bottles are commonly used. By mixing fluor spar and pieces of glass or fine sand, and acting upon the mixture by strong sulphuric acid, an acid gas is given off, this is fluosilicic acid = $SiFl_3$, which, together with hydrofluoric acid, combines with water, and is termed *hydrofluosilicic* acid = $3HFl + 2SiFl_3$. This solution is occasionally used in the laboratory as a test for potash and soda.

Silicium (Si 213).

Silicium is a light brown powder. It is one of the most extensively diffused elements in nature, but it always exists in combination with oxygen, forming silica or silicic acid = $Si\,O_3$.

The substances known as *flints*, *agates*, *quartz*, *sand*, &c., are nearly pure silica, and every other earthy substance in nature contains more or less silica combined with it. This substance is of essential importance to the potter and glass maker, but it is of little consideration in dyeing.

Boron (B. 10·9).

Boron is a solid, and generally obtained as a greenish brown powder, destitute of metallic lustre. It is not found in nature except in combination with oxygen, with which it forms boracic acid $= BO_3$. This acid combines with bases forming borates; but it is found in nature uncombined, especially among the volcanic products of the Lipari islands. The principal sources of the compounds of boron are, however, some springs in India, and the waters of Sasso, which hold in solution a quantity of borate of soda (borax). In some lakes in the neighbourhood of volcanoes there are also great quantities of boracic acid. These waters are concentrated by evaporation sufficiently to allow the acid to crystallize, and in this state it is known in commerce as raw borax. Arrived in this country it is dissolved and saturated with soda to form borate of soda, which is obtained in large crystals; this is the refined borax of commerce, and the principal compound of boron known in the arts. It is much used in medicine and as a flux in the operations of metallurgy.

Carbon (C 6).

Carbon is very extensively diffused through nature, and the complete description of this element and its compounds would embrace the whole chemistry of organic matter. It is met with also in various forms and combinations in the mineral kingdom. Carbon exists pure in diamond and coal, and forms nearly the whole of plumbago and graphite (popularly *black lead*). It may be obtained by submitting either animal or vegetable matter to a high heat in a close vessel: the oxygen, hydrogen, and nitrogen of these bodies pass off, and the carbon is left. Charcoal is therefore carbon with a little earthy matter; and coke, ivory black, and lamp black, are other familiar names for it in an impure state. These substances

differ in character from each other in having different proportions of earthy ingredients in combination or mixture with the principal element. Carbon is infusible, therefore we only know it in a solid form. It possesses many singular properties connected with the principles of dyeing; some of these we will state here and reserve the applications till we come to consider the methods and theory of dyeing.

Carbon has the property of absorbing gases within its pores. One cubic inch of the best charcoal made from boxwood has been found to absorb or imbibe the following quantities of the different gases named:—

Cubic inches.	
90	Ammoniacal gas.
85	Hydrochloric acid gas.
65	Sulphurous acid.
55	Sulphuretted hydrogen.
40	Peroxide of nitrogen.
35	Carbonic acid.
9	Oxygen.
7	Nitrogen.
1.7	Hydrogen.

This curious property is not well understood; it is generally supposed that it results from the powerful cohesive attraction between the gas and the surface of the charcoal by which the gas is liquified. Somewhat analogous to this property is its power of absorbing or imbibing colouring matters, and on this account it is extensively used for discolouring sugar; charcoal has also the property of keeping water sweet for a long time. The various kinds of charcoal possess this discolouring power differently, probably depending on their state of purity. Supposing that the substance to be discoloured is sulphate of indigo, the following are the powers of some kinds of charcoal compared with that of charcoal from bones, which we call 1.

Lamp black.....= 4
Charcoal from starch, ignited with potash .....=12
Lamp black, ignited with carbonate of potash ..=16
Ivory black, ignited with carbonate of potash ..=45
Blood charcoal, ignited with carbonate of potash =50

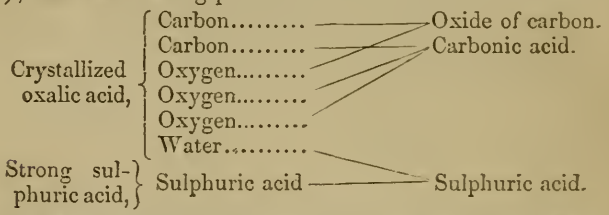
This property of absorbing colours is also considered an attraction of surface, and it is found in some cases to be

sufficiently strong to overcome chemical affinity. The same property of imbibing colours is possessed by other porous matters to some extent, and the porous nature of the fibre of cotton, woollen, and silk, may exercise an influence of a similar kind, a subject which we intend to consider further on.

Carbon combines with oxygen in three proportions, forming:

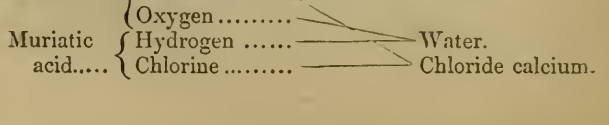
Carbonic oxide.....CO.
Carbonic acid.....CO_2.
Oxalic acid.....C_2, O_3.

Carbonic Oxide is obtained by heating together strong vitriol and crystallized oxalic acid. This operation may be performed in a retort or flask, as described for hydrogen (page 38); the action taking place is—



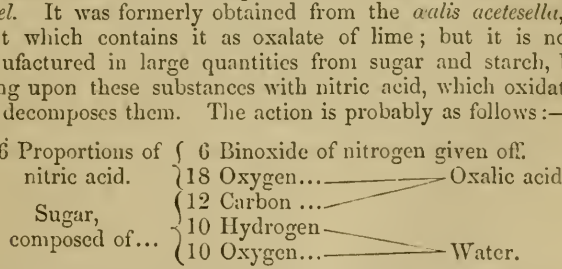
The action is simply the sulphuric acid taking the water from the crystallized oxalic acid and setting the elements free. By passing the gases through a solution of caustic potash or lime water, the carbonic acid is absorbed, and carbonic oxide is obtained pure. It is a colourless gas, inodorous, and burns with a blue flame. It is the presence of this gas which gives the blue flame of a coke fire. The product of its combustion is carbonic acid.

Carbonic Acid.—When carbon is brought to a red heat, it burns and dissipates; the oxygen combines with the carbon, and produces gaseous carbonic acid. This gas is generally obtained for experiment from its compounds. Thus, when a few pieces of marble or chalk are put into a flask or retort, and some dilute muriatic acid is added, effervescence takes place, and the action is—



Carbonic acid is absorbed by water, in quantity equal to the volume of the gas; but the materials from which it is prepared are so cheap, that this absorption does not signify much in an experiment. The gas is colourless, and heavier than atmospheric air, so that it may be poured from one vessel to another as if it were a liquid. A light is instantly extinguished by immersion in an atmosphere of it, and an animal soon dies if kept in air containing nine per cent of it. Combined with water, it manifests acid properties, and gives the water an agreeable taste and pungency, as experienced in aërated waters. It combines readily with alkaline and earthy bases, producing carbonates. Its affinity for lime is very great; but it is liberated from all its compounds with effervescence by a stronger acid. When the dry gas is passed over redhot charcoal, it is decomposed; the charcoal combines with half its oxygen, and forms oxide of carbon.

Oxalic Acid has been long known in commerce as *salt of sorrel*. It was formerly obtained from the *oxalis acetesella*, a plant which contains it as oxalate of lime; but it is now manufactured in large quantities from sugar and starch, by acting upon these substances with nitric acid, which oxidates and decomposes them. The action is probably as follows:—



The acid crystallizes with water, which, as has been shown above, is essential to its existence. It combines with bases, and forms salts of great importance in the laboratory. Thus the oxalates of potash and ammonia are excellent tests for lime; and they are also of some importance in the dyehouse, as are also the oxalates of tin, &c. Oxalic acid is easily distinguished from any of the alkaline and earthy salts such as the sulphate of magnesia (epsom salts), for which it has occasionally, through ignorance, been mistaken by its strong acid character. It is easily detected by heating it to redness upon a piece of platinum, when it will all evaporate, and leave no residue, while the magnesian salt does. It sometimes contains nitric acid, peroxide of nitrogen,

and epsom salts: the two first may be detected by dissolving a little of the acid, and adding a minute colouring of sulphate of indigo, and then boiling: the presence of these impurities decolours the indigo. The presence of epsom salts may be detected by chloride of barium, or by evaporation as directed above. There is often about one per cent. of this salt in the commercial oxalic acid.

This acid has been long used in the dyehouse, and acts powerfully upon many substances, but it is not now so generally used. A curious salt, of a beautiful colour, may be obtained by taking

One part of bichromate of potash,
Two of binoxalate of potash,
Two of oxalic acid;

and dissolve the whole together in hot water, when carbonic acid is evolved, and a double salt of oxalate of potash and chrome, having a fine purple colour, is formed in solution. Crystals of the salt, possessing a very deep blue colour, may be obtained by evaporation.

Cyanogen.—Carbon combines with nitrogen, and forms cyanogen, a very important compound, consisting of one equivalent of nitrogen, and two equivalents of carbon $= C_2N$. It is a gas, and has the property of combining with other elements as if it were itself an element. It belongs, therefore, as was stated at p. 33, to the class of compounds known as salt radicals. It is not obtained by directly bringing nitrogen into contact with carbon, but by the decomposition of animal compounds in contact with metallic bases, as we will have occasion to describe further on. The gas is generally obtained for experiment from its salts, by heating cyanide of mercury in a retort. The mercury runs over in a metallic state, and the cyanogen escapes as gas, and may be caught at the pneumatic trough. Cyanogen combines with oxygen, and forms an acid called cyanic acid, and this combining with bases, forms *cyanates*.

Cyanogen combines also with hydrogen, and forms an acid termed hydrocyanic acid, or more commonly prussic acid, which, like hydrochloric acid, does not combine with bases, as $CN_2 + H$, and although certain salts are termed prussiates,

they are properly cyanides. Some of them are highly important in the arts, and will be noticed in their proper places.

Cyanogen also combines with the metals in the same manner as chlorine and iodine, and forms that class of salts termed *cyanides.**

Mellon.—Carbon combines with nitrogen in other proportions besides that of cyanogen. There is one expressed by N_4C_6, which is a solid substance of a lemon yellow colour, insoluble in water, but which acts the part of a salt radical, and combines with hydrogen to form an acid which also combines with several of the metallic bases. This salt radical is termed MELLON, and the salts from it are termed *mellonides;* but these compounds are not so well known as the cyanides, and they are less useful.

Carbon combines with hydrogen in various proportions, forming different kinds of gases, such as *light* carburetted hydrogen $= CH_2$; olefiant gas $= C_4H_4$; common coal gas, and some other hydrocarbons consist of those gases as constituents. Carbon also combines with sulphur, and forms with it a colourless, volatile, and inflammable liquid, possessing a most putrid smell: this is sulphuret of carbon. In organic bodies, carbon is combined with oxygen, hydrogen, and nitrogen, in an endless variety of proportions. Some of these compounds will be brought under notice when treating of the organic substances which fall within the scope of our subject.

* The distinction between the names ending in *ate* and *ide* must here be borne in mind.

METALLIC SUBSTANCES.

General Properties of Metals.

We now proceed to consider that division of the elements commonly known as metals. To define the peculiar properties of a metal is somewhat difficult, for whichever property we select, it is either absent in some metal, or it is possessed by some non-metallic element. A few of the more prominent physical properties may, however, be named.

1st, They all possess a peculiar lustre. 2d, They all reflect light, which is the cause of that lustre. 3d, They are all fusible by heat, and while in fusion retain their lustre. 4th, They are all conductors of light and heat. 5th, They have all to a certain degree the property of extension; they are *malleable* under the hammer; and *laminable* under the roller; and being capable of extension by drawing into wire, they are termed *ductile.*

There are also chemical distinctions which are much more universal. They are all *basic*, that is to say, capable of combining with oxygen, and forming oxides; and with acids they form a series of compounds termed salts, of which the metal is termed the *base.* It is on account of the possession of these general properties that hydrogen is regarded as a metal in a gaseous state: it is pre-eminently basic.

When metals combine with one another the compound is termed an alloy. Brass is a chemical mixture of copper and zinc; and German silver is a like mixture of copper, zinc, and nickel; both brass and German silver are therefore alloys. Alloys retain most of the physical properties of the metals of which they consist. A great many of the recently discovered metals are very rare, and have only been found in certain localities, and in minute quantities. The alkalis and earths were long looked upon as elements; they had never indeed

been decomposed till 1807. What was until that time known as the element

Potash, we now know to be the oxide of the metal Potassium.
Soda, ... Sodium.
Lithia, ... Lithium.
Lime, ... Calcium.
Barytes, ... Barium.
Magnesia, ... Magnesium.
Alumina (pure clay), ... Aluminum.

Potassium (K 39·2).

Sir H. Davy decomposed potash by a powerful electric current, and demonstrated it to be the oxide of a peculiar metal which he termed potassium. This metal may be obtained easily by roasting a quantity of bitartrate of potash (cream of tartar) in a covered crucible: the immediate product is what is termed *black flux;* then mixing this matter with a quantity of finely ground charcoal, and putting the whole into a wrought iron bottle, and distilling it at a high heat, the metal comes over, and is caught in a vessel containing naphtha, a fluid that contains no oxygen. Only such a fluid can be used for this purpose, as the attraction of potassium for oxygen is so great, that it decomposes all substances which contain that element.

Potassium is a white metal, with a lustre somewhat like silver; at ordinary temperatures it is soft, and may be flattened between the fingers, but at 32° it is hard and brittle. It melts at 136°. When exposed to the air it becomes covered immediately with a white crust of oxide. It is lighter than water, and when thrown upon that fluid it swims, and instantly bursts into flame, combining with the oxygen of the water so rapidly, as to produce heat sufficient to kindle the hydrogen as it makes its escape. The metal not only fuses, but a small portion of it goes off as vapour, and burning with the hydrogen produces a beautiful red-coloured flame. In this experiment potash is formed in the water. Pure potash is the oxide of the metal potassium, but it is not prepared from the metal for manufacturing purposes.

Potash.—Sometimes termed the *vegetable alkali*, takes its name from being prepared for commercial purposes in iron pots. When a piece of wood, or other vegetable substance is slowly burned until all inflammable matters are consumed, there is left a white substance called *ash*. This ash consists of the mineral ingredients of the vegetables, along with potash, lime, and other earthy ingredients. The potash and other soluble ingredients are extracted by treating the ash with water.

The average quantity of ash obtained from wood is about one per cent. In America, where wood is an incumbrance, it is felled, piled up in masses, and burned for the manufacture of potash. The ashes of the wood are collected and put into cisterns provided with false bottoms, and run-off plugs underneath. A quantity of water is thrown upon the ashes in a cistern, and after stirring and settling a few hours, all the soluble matters are dissolved, and the liquor is drawn off, evaporated to dryness, and the residue afterwards fused at a red heat into compact masses, and in this state constitutes the commercial *black ash*. As other matters besides the potash are soluble in water, the black ash thus prepared contains these substances as impurities. These are mainly sulphites, sulphurets, and chlorides of potash, along with some earthy matters.

Pearl ash is prepared by calcining the black ash in a reverberatory furnace until all the carbonaceous matters and the sulphur are driven off. The remaining mass is then dissolved in water, and the solution evaporated to dryness in large iron pans. Towards the conclusion of the process the mass is stirred to give it a lumpy granulation. This ash contains much less extraneous matter than black ash, and is consequently weaker as an alkali. It is more fully carbonated. Dr. Ure states (Dictionary of Arts, &c.) that he found the best pink coloured Canadian potash to contain 60 per cent. of real potash, while the best pearl ash contained only 50 per cent. These are the two states in which potash is introduced into the dyehouse. The methods for testing the quantity of real alkali they contain will be given when we come to speak of soda.

The principal use of potash is to destroy or take off any grease or oil which may exist in or upon the fibre to be dyed, and it does this by combining with these substances and form-

ing soap, which, being soluble in water, is easily removed. Dyers are often in the habit, when about to steep or boil their goods, of simply adding to their solution or boiler, some pearl ash or potash, but as the alkali is in union with an acid (carbonic acid) forming a carbonate, its power of combining with oil or grease is to a great extent neutralized. The white obtained upon the fabric may be good enough, and as was before remarked when speaking of chlorine, a good white can be got without potash; but it is not so permanent. If grease or oil be present they are not removed, but only concealed, and the dyer is often annoyed by large resist spots which he cannot account for, and which are not so easily removed after the goods are boiled as before. The alkali, whether pearl or potash, before being used ought to be made caustic, that is, deprived of its carbonic acid, and converted into oxide of potassium. This is done by boiling the carbonated alkali with newly slaked lime; the lime combines with the carbonic acid of the alkali, and falls to the bottom, while the caustic alkali remains in solution. Without detailing the various methods practised, some of which are not good, we shall rather give what we consider the best. The carbonate of potash ought to be dissolved in not less water than six times its weight; it is better, however, to use ten times its weight, as if a less quantity of water be used, the potash is not deprived of all its carbonic acid. The reason assigned for this singular phenomenon is, that both caustic potash and its carbonate have a strong affinity for water, and when less than six times its weight is used, there is sufficient water to supply the carbonate, but not the caustic alkali, and hence the carbonate is not converted into the caustic state. The exact quantity of lime is not material, provided there be enough. The lime ought to be added when the alkali is boiling, and from time to time, until, a little of the solution being taken out, it does not effervesce by the addition of a little dilute sulphuric acid. If strong acid is used, care must be taken before adding it that the solution be cold, for if not, it will spurt, and may injure the manipulator. The best way is to take a little of the alkali and dilute it with cold water, and then add the acid. When there is no effervescence, the alkali is caustic. The boiling is then stopped, and when the lime settles the clear is taken off and kept in an iron vessel covered closely,

as the potash readily takes up carbonic acid from the air. For bleaching, and other cleansing operations, and also for many purposes in the dyehouse, the supply should be taken from this stock vessel. It will be necessary, however, that the operator know the exact strength of the solution, in order that he may know the proper quantities of it he ought to use for particular purposes. On this point a pretty correct approximation is obtained by knowing the per centage of pearl or potash used in making the solution, and then calculating the quantity to each gallon: but greater exactness is attained by using the following table, (drawn up by Dr. Dalton,) in which the specific gravity is supposed to be known, and hence the quantity present of the alkali in solution:—

Potash per cent. in solution.	Specific gravity of solution.	Specific gravity by Twaddell's.	Boiling point of solution.
72·4	2·000	200°	600°
63·6	1·880	176	420
56·8	1·780	156	360
51·2	1·680	136	320
46·7	1·600	120	290
42·9	1·520	105	276
39·6	1·470	94	265
36·8	1·440	88	255
34·4	1·420	84	246
32·4	1·390	78	240
29·4	1·360	72	234
26·3	1·330	66	229
23·4	1·280	56	224
19·5	1·230	46	220
16·2	1·190	38	218
13·	1·150	30	215
9·5	1·110	20	214
4·7	1·060	12	213

In the first column of this table the percentage of alkali is given by weight. Thus a gallon of water is 10lbs. weight, therefore a gallon of the caustic ley solution will have one-tenth part of the potash indicated by the table according to the specific gravity. Say the solution stands 30° by Twaddell,—the percentage of this is 13, and this divided by 10 gives 1·3

lb. = 11lb. 5oz. nearly of caustic potash to a gallon of the ley. The stock ley should not be made stronger than this.

In the last column the boiling points of the solution at different strengths are entered. These numbers are important, and explain to some extent why boiling by steam is not so effective as by fire; for the steam heat, as was stated at page 7, is not higher than 210°, whereas the lowest temperature noted in the table is 213°.

Potash, as used in the dyehouse, is never chemically pure. Even when used as caustic, it generally contains lime and soda, and often their sulphurets. Lime may be detected by adding a little clear solution of carbonate of potash to a clear solution of the caustic potash, when its presence will be known by the milkiness produced. It is not, however, detrimental to the dyer in the operations in which potash is commonly used. Sulphurets may be detected by adding to a dilute solution of the potash some acetate of lead; if a sulphuret is present, there will be a blackish precipitate. Sulphurets are destructive to gold ornaments on muslin and other cloths, for the metal is rarely pure; commonly it is an alloy of gold with copper, &c., and sometimes the inferior metal is merely gilt. The sulphuret acts upon all the inferior metals by contact, and at least blackens them. Potash containing sulphurets should therefore be avoided for goods having such ornaments.

Caustic potash is evaporated to dryness, fused, and poured into moulds to form it into small cylinders; in this state it is sold by druggists under the name of *stick-potash*.

Potash has a strong affinity for water, and deliquesces rapidly when exposed to the air; this property is also possessed by the carbonates.

The following table gives the average quantity of pure alkali, &c., in the different sorts of commercial potash:—

Name of Place from which it is procured.	Real Potash	Sulphate of Potash.	Muriate of Potash.	Carbonic Acid and Water.	Insoluble Ingredients.	Total.
Potash of Russia, ..	772	65	5	254	56	1152
— America, ..	857	154	20	119	2	1152
American Pearl,...	754	80	4	308	6	1152
Potash of Treves,..	720	165	44	199	24	1152
— Dantzic,....	603	152	14	304	79	1152
— Vosges,.....	444	148	510	304	34	1440

Potassium combines with chlorine, and forms chloride of potassium—more commonly termed muriate of potash; which may be prepared by adding hydrochloric acid to caustic potash, or its carbonate. It combines also with iodine, and forms iodide of potassium (page 100); with bromine it forms bromide of potassium; and with sulphur it forms the sulphuret, or sulphide of potassium. We have already noticed most of these salts.

Sulphate of Potash.—When sulphuric acid is added to potash it forms a salt which has neither acid nor alkaline properties, and which is easily crystallised. This neutral salt is produced abundantly in the manufacture of nitric acid from nitre. It is not deliquescent, and requires 15 times its own weight of water to dissolve it.

Bisulphate of Potash.—This salt is also obtained like the sulphate in the process of making nitric acid from nitre; but it may be prepared by adding to the sulphate half its weight of sulphuric acid, and bringing the mixture up to a red heat in a porcelain or platinum vessel. This salt has strong acid reactions, is very soluble in water, melts easily with heat, and is exceedingly useful for dissolving metals, many of which may be dissolved by it easily, although of very difficult solution in the pure acid.

Sulphite of Potash is prepared by passing a current of sulphurous acid gas through a solution of carbonate of potash till saturated. It crystallises, and should be kept close, as it rapidly passes to the state of sulphate by exposure to the air.

Nitrate of Potash may be prepared by saturating potash with nitric acid; but it is obtained abundantly in native beds (page 52). It is prepared artificially in Germany and France, by forming large beds of animal and vegetable refuse, in which decomposition is effected by putrefaction. Potash is present in the organic matter, and these also yield nitrogen and oxygen to form nitric acid; and by combination the nitrate of potash is formed. The chief uses of nitrate of potash are in the manufacture of gunpowder and nitric acid.

Chlorate of Potash is prepared by passing chlorine gas through carbonate of potash. When the solution is saturated, crystals of this salt are formed (page 61). This salt, as already stated, is advantageously used in several operations in the dyehouse, in which oxidation is required; also with

decoctions of some of the woods. When mixed with substances containing carbon, it gives them great combustibility. Thus, if a drop of sulphuric acid is added to a mixture of chlorate of potash and sugar, combustion instantly commences, and the mixture burns with great rapidity.

Phosphate of Potash.—This salt is obtained by adding carbonate of potash to a hot solution of phosphoric acid, until the solution ceases to redden blue litmus paper. By careful evaporation, the salt may be crystallized.

If the carbonate of potash be added to the phosphoric acid while cold, in sufficient quantity to saturate it, the solution, by evaporation, gives crystals of a salt having two proportions of acid—a biphosphate of potash.

Oxalate of Potash.—This salt is obtained by saturating carbonate of potash with oxalic acid, and crystallizing. In this state it contains one proportion of water.

The *Binoxalate* is obtained from wood sorrel, in which it exists ready formed. It is obtained by reducing the expressed juice of the sorrel to the consistence of a syrup, and setting it aside to crystallize. It is sold as *salt of sorrel* and *essential salt of lemons*. The taste of the salt is acid; it is employed for removing ink stains from goods and recently formed iron moulds. Its crystals are composed of 2 acid, 1 potash, and 2 water.

Ferrocyanide of Potassium.—This salt is known as yellow prussiate of potash. We have already referred to the compound salt radical termed cyanogen, and stated that it combines with other bodies, and forms salts resembling the chlorides; but it is occasionally found that two such salts group together and form a distinct compound. Thus, one proportion of the protocyanide of iron = Fe, Cy, combines with two proportions of cyanide of potassium, = 2Cy K, and forms the *ferrocyanide of potassium*. These two proportions of potassium may be replaced by another metal, but the iron and the three equivalents of cyanogen maintain themselves together. It has, therefore, been inferred, that Fe Cy_3 is a distinct salt radical, which may be termed *ferro prussic acid;* a theoretical deduction very interesting to study, and which will be more fully developed as we proceed. The salts formed by this acid are distinguished by the prefix *ferro*.

The ferrocyanide of potassium, or prussiate of potash, is pre-

pared on the large scale by calcining together dried blood, hoofs, horns, hides, old woollen rags, or similar materials, with carbonate of potash, in an iron vessel: commonly those substances are partially carbonized or burned in large cast-iron cylinders previously to being mixed with the potash. If the animal matters are used without being subjected to this preliminary process, they are mixed in the ratio of about 8 to 1 of pearl ash; but if burned previously, one and a half of the charcoal is mixed with one of pearl ash. When the animal matters are used without being charred, the calcining pot is left open to allow the materials to be stirred and the noxious vapours to escape; after which the vessel is closed, and the heat is increased. This is continued for some time, and at intervals of half an hour, the mouth of the vessel is uncovered for the purpose of stirring the matter within. This process is continued until the flame ceases to rise from the surface, and the materials are reduced to a red semifluid mass, which generally takes place in about eight hours after the pot is closed. From this description, the nature of the action is easily understood. The animal matters which contain nitrogen and carbon abundantly, are decomposed by the heat; but, on account of the presence of the iron and potash, definite portions of the elements combine and form cyanogen, which is simultaneously taken up by the potassium and iron, and we have two proportions of cyanide of potassium, with one proportion of cyanide of iron. The molten mass is scooped out with iron ladles, and allowed to cool. When the mass has cooled, it is dissolved in cold water, and the solution is filtered through cloth. Lest any cyanide of potassium should remain which had not received the proportion of iron, sulphate of iron (copperas) is added by degrees to the solution, so long as the prussian blue which is at first formed on adding the iron salt is redissolved. The whole is then evaporated to a proper consistency; after which, pieces of coarse cord are suspended throughout the liquid, upon which crystals of ferro-prussiate are formed in regular bunches, of a beautiful light citron yellow.

Ferrocyanide of potassium crystallizes with three proportions of water, which it loses at 212°. It dissolves in 4 parts of cold and 2 parts of boiling water. From this salt all other ferrocyanides are derived as precipitates; those of the metals are formed by adding a salt of the metal to a solution

of the prussiate. The following are the appearances of a few of those precipitates, corresponding to the metals employed:—

Protoxide of Manganese	White, turning to a deep red.
Peroxide of Manganese	Greenish grey.
— Lead	White, with a yellowish hue.
Peroxide of Iron	Deep blue.
Protoxide of Iron	White, turning blue by exposure.
— Copper	Brown.
— Zinc	White.
Protoxide of Tin	White.
Peroxide of Tin	Yellow.

Each of these precipitates is a ferrocyanide of the metal used, which has taken the place of the potassium; they are all insoluble in water, and where a colour can be obtained by them, they are suitable for a dye, although the colours dyed by the yellow prussiate are fugitive. Every alkaline substance, such as soap, destroys them, and they are easily affected by that universal creator and destroyer of colours, the sun.

The principal use of the ferrocyanide salt in the dye-house is for dyeing Prussian blue. To dye this colour, the goods are impregnated with a persalt of iron, and then passed through a solution of yellow prussiate of potash; but this mode is objectionable for light shades and light goods, as it causes much loss of the Prussian salt. The general method of dyeing light Prussian blues upon cloths is, to put a little nitrate of iron into a vessel full of water; the cloth is wrought in this for about ten or fifteen minutes, and then washed through two or three tubs full of clean water, to take off all the superfluous acid and iron. Whether the cause of the reception of the dye be an attraction of the material of the cloth for the iron, or the simple power of absorption of the fibres, we shall not stay to examine here; but although the nitrate of iron is an exceedingly soluble salt, a portion of the peroxide of iron remains fixed in the fibres, having abandoned its acid, and this no washing will remove. The cloth, being well washed from the acid, is put into the prussiate. A small quantity of acid must be added to the ferrocyanide of potassium solution, to take up the potassium, and to set the ferrocyanogen at liberty, to unite with the iron upon the cloth,

this forms ferrocyanide of iron or Prussian blue, and constitutes the dye. Considerable care ought to be taken in adding acid to the prussiate, otherwise the colour is liable to change, becoming grey or reddish when dried.

The following mode of adding sulphuric acid to the prussiate, when a considerable quantity of goods are to be dyed at once, is commonly practised. What is considered the proper quantity of yellow prussiate of potash is dissolved in just as much boiling water as is necessary for solution. To this solution a quantity of sulphuric acid is added, sufficient to make it strongly acid; and the mixture thus prepared is added to the *prussiate tub* as required. This method of adding the sulphuric acid is exceedingly objectionable, as it causes the evolution of prussic acid, which may be detected by the pungent smell it excites; and in proportion to the escape of that gas, there is a loss of the dyeing power of the prussiate. If three parts of acid be added to seven of yellow prussiate, the loss would amount to one-half, and the remaining half would be so changed in its properties as to produce only a bad blue. Thus the dyer must use an additional quantity of prussiate, and after all he produces but an indifferent colour.

The proper method of using the acid is to dissolve the prussiate in hot water, and to add the necessary quantity of this solution to the water-tub in which the goods are to be dyed. Previously to putting in the cloth, a few drops of sulphuric acid are added, just sufficient to be perceptible to the taste; or, what is a much better test, sufficient to redden blue litmus paper. The goods being wrought for some time in this mixture, they are washed in clean water, having a small quantity of alum in solution. For light shades of sky-blue, they should not be dried from the alum solution, as there is a great tendency to assume a lavender hue. A better plan is to employ two tubs of water, the one being touched with alum, and the other pure, for washing from it. Cloths dyed by the prussiate should be exposed to a very dry atmosphere when hung up to be dried.

Deep blue is dyed by passing the goods through strong nitrate of iron, then through potash ley, which fixes the oxide of iron upon the cloth, and then through the prussiate.

Royal blue is dyed by adding protochloride of tin (*salts of tin*) to the nitrate of iron; entering the goods immediately,

and passing them from the iron through the prussiate without washing. This method gives a rich deep blue, and is now much practised. Some of the peculiarities of the process will hereafter be described; meantime, it will be sufficient to observe, that a peculiar purple bloom is given, by using hydrochloric acid in the prussiate solution instead of sulphuric acid.

Ferricyanide of Potassium.—This is the red prussiate of potash. If a current of chlorine gas be passed through a strong solution of yellow prussiate of potash, till the solution changes to a reddish colour, and when a drop of it added to nitrate of iron gives no precipitate, there is formed chloride of potassium, and a salt differing materially from yellow prussiate. The solution being evaporated, this salt is obtained in beautiful ruby-red crystals, termed, from their colour, red prussiate of potash. They are anhydrous, soluble in 4 parts of cold and a less quantity of hot water. The red prussiate is well adapted for many operations in dyeing, but it is too expensive for general use. It yields the following colours with the salts of the different metals undernamed :—

Bismuth	Pale yellow.
Cadmium	Yellow.
Cobalt	Dark-brown red.
Copper	Yellowish-green.
Protosalts of iron	Deep blue.
Persalts of iron	No precipitate.
Manganese	Brown.
Mercury	Red-brown.
Nickel	Yellow-green.
Tin	White.
Zinc	Orange-yellow.

It will be observed from this table, that the salts of iron, which yield a blue with yellow prussiate of potash, give no colour with the red prussiate; and the protosalts of iron, which give only a grey with yellow prussiate, yield a deep blue with red prussiate.

The true constitution of this salt, or rather the arrangement in which these elements unite, is still subject of hypothesis. We have seen, in regard to the *ferrocyanide*, that the iron exists as a protocyanide, with two cyanides of another metal;

but in the *ferricyanide* we have iron as a percyanide, with cyanides of other metals. Thus—

Ferrocyanide.....$Fe\ Cy + 2\ Cy\ K$ = Protocyanide.
Ferricyanide.....$Fe_2\ Cy_3 + 3\ Cy\ K$ = Percyanide.

Those who suppose that the compound $Fe\ Cy_3$ of the yellow prussiate forms the salt radical of all the ferrocyanides, suppose also that the red prussiate has $Fe_2\ Cy_6$, consisting of the same number of elements combined together in double proportions, corresponding to the *pro* and *per* oxides of iron. But whatever may be the true relation in which the elements are united, the two salts are distinct in their reactions, and we would suggest to the dyer to give particular attention to the difference of the salts, with reference to salts of iron, as they are important, and will be referred to hereafter.

Cyanide of Potassium.—If yellow prussiate be dried at a heat of about 220° to 300°, and 8 parts of this dried salt be mixed with 3 parts of dry carbonate of potash and the mixture put into a crucible, and fused until effervescence ceases, then removed from the fire, and allowed to settle for a few minutes: by pouring off the clear into an iron vessel, it solidifies into a white crystalline mass which is cyanide of potassium = Cy K. This salt has a strong alkaline reaction, and is peculiar for its power of dissolving metals and giving precipitates which might be advantageously applied to some of the operations of dyeing.

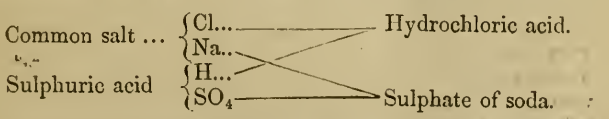
Cyanate of Potash.—This salt is prepared in the same way as the last, but with the addition of some oxide of manganese, or other oxide, which converts the cyanogen into cyanic acid, and forms cyanate of potash = Cy O, KO. The cyanates of the alkalis are all soluble in water, and in this they differ from the cyanates of the other metals.

Sodium (Na 23.)

Soda was not distinguished from potash till near the middle of the eighteenth century, when their distinctive characters were recognised. The potash was termed the vegetable, and the soda the mineral alkali. In 1807, Sir H. Davy demonstrated that soda, like potash, is the oxide of a metal which he named *sodium*. It is a white metal, having much the ap-

pearance of silver, but is sufficiently soft to yield to the pressure of the fingers, and to be cut by the nail. It oxidates spontaneously in the air, but not so rapidly as potassium. When a small piece is thrown upon water, it floats; the heat, generated by combining with the oxygen of the water, melts it, and it forms a silvery globe, which gyrates rapidly on the surface of the water; but it does not inflame the hydrogen unless it be kept stationary, and then an explosion takes place. If, however, the temperature of the water is as high as 110° Fah., the hydrogen burns as it is evolved, with a bright flame. In these experiments oxide of sodium is formed and dissolved in the water, which thus becomes a solution of *caustic soda*. Sodium is a very abundant element in nature, but is always found in combination, *e. g.*, as nitrate of soda, and chloride of sodium (common salt). This last is the great source of soda for manufacturing purposes; and since the process of making soda from it was discovered, this alkali, owing to its cheapness, has been used instead of potash in almost all the processes of the arts that admit of the substitution.

Soda, as sold to dyers and bleachers, is in the state of a dry white powder, or granular substance, termed *soda-ash*, which is an impure carbonate prepared as follows:—A quantity of about 600 lbs. of common salt is put upon the bottom of a reverberatory furnace, previously heated; upon this is let down, from an apparatus on the roof of the furnace, a quantity of sulphuric acid, of the specific gravity 1·600; and the salt is decomposed. The result is as follows:—



The hydrochloric acid passes off with the steam occasioned by the dilute sulphuric acid. This operation, during which the materials require to be stirred occasionally, lasts about four hours: the charge is then withdrawn from the furnace. The sulphate of soda thus prepared, is reduced to powder, and mixed with an equal weight of ground chalk, and half its weight of coal, well ground and sifted. This mixture is introduced into a very hot reverberatory furnace, about two hundred weight at a time, and is frequently stirred until it is

uniformly heated. In about an hour it fuses; it is then well stirred for about five minutes, and drawn out with a rake into a cast iron trough in which it is allowed to cool and solidify. This is called ball soda, or British barilla, and contains about 22 per cent. of alkali. To separate the salts from insoluble matter, the cake of ball soda when cold, is broken up, put into vats, and covered by warm water. In six hours the solution is drawn off from below, and the washing repeated about eight times, to extract all the soluble matter. These liquors being mixed together, are boiled down to dryness, and afford a salt which is principally carbonate of soda, with a little caustic soda and sulphuret of sodium. For the purpose of getting rid of the sulphur, the salt is now mixed with one-fourth of its bulk of sawdust, and exposed to a low red heat in another reverberatory furnace for about four hours, which converts the caustic soda into carbonate, while the sulphur is carried off. This product, if the process is well conducted, contains about 50 per cent of alkali, and forms the soda-ash of the best quality. When it is to be converted into crystallized carbonate of soda, it is dissolved in water, allowed to settle, and the clear liquid boiled down until a pellicle appears on its surface. The solution is then run into shallow boxes of cast iron to crystallize in a cool place, and after standing for a week, the mother liquor is drawn off, and the crystals drained and broken up for the market. This mother liquor is evaporated to dryness, and yields a very impure soda-ash, containing about 30 per cent. of alkali, which is often employed for making soap.

The common crystallized carbonate of soda of the shops is very pure, but is crystallized with 10 equivalents of water. When exposed to the air, these crystals lose a portion of their water, and assume a chalky white appearance; if they are subjected to heat, they melt in their water of crystallization. We have known these crystals used for the operations of bleaching merely dissolved; but they are neither good nor profitable used in this way.

They contain in 100 parts by weight

Caustic soda,.....	21·81
Carbonic acid,.....	15·43
Water,.....	62·76
	100·00

Thus fully more than three-fifths of their weight is water.

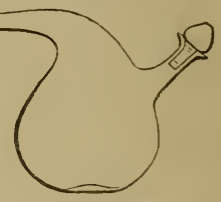
The dry carbonate of soda of the shops, so much used for domestic purposes, is the same as the crystallized soda deprived of its water of crystallization.

Soda-Ash.—Owing to various circumstances attending the manufacture of this salt, its per centage is very uncertain, varying from 40 to 50 per cent., and it is, therefore, generally priced according to its per centage. The per centage may be determined by some such means as we have described for bleaching powder, that is, by having an acid exactly of the strength at which 100 measures of it will saturate 100 grains of caustic soda. To form the test acid, according to Professor Graham's directions, 4 ounces avoirdupois of oil of vitriol are diluted with 20 ounces of water, or larger portions of acid and water may be mixed in these proportions. About three-fourths of an ounce of bicarbonate of soda is heated strongly by a lamp for a few minutes to obtain pure carbonate of soda, (or what will do, take some crystals of soda and dry in a basin until all water is given off; when boiling has ceased, make the heat to about a dull red, this will give the soda salt,) of which 171 grains are immediately weighed, that quantity containing 100 grains of soda; this portion of carbonate of soda is dissolved in 4 or 5 ounces of hot water, and the alkalimeter is filled up to the highest graduation with the dilute acid. The acid is poured gradually into the soda solution till the action of the latter upon blue litmus test-paper ceases to be alkaline and becomes distinctly acid, and the measures of acid necessary to produce that change are accurately observed; say it requires 90 measures. A plain cylindrical jar, of which the capacity is about a pint and a half, is graduated into 100 parts, each containing 100 grain measures of water, or ten times as much as the divisions of the alkalimeter. This jar is filled up with the dilute acid to the extent of 90, or whatever number of the alkalimeter divisions of acid were found to neutralize 100 grains of soda, and *water* is added to make up the acid liquid to 100 measures. This forms a test acid of which 100 measures neutralize and are equivalent to 100 grains of soda, or one measure of acid to one grain of caustic soda. This acid ought to be kept in a well-stoppered bottle. By a curious coincidence, strong oil of vitriol diluted

with 11 times its weight of water, gives this test acid exactly; but, as oil of vitriol varies a little in strength, it is better to form the test acid in the manner described, than to trust to that mixture. Twenty-one measures of the test acid should neutralize 100 grains of crystallized carbonate of soda, and 68·5 measures of it should neutralize 100 grains of pure anhydrous carbonate of soda.

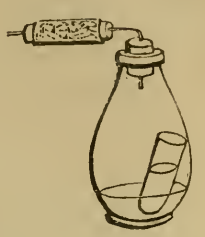
To test a sample of soda-ash, 100 grains are weighed and dissolved in two or three ounces of hot water. The alkalimeter is filled with the test acid, which is gently poured into this solution, stirring, as each drop is added, until a piece of blue litmus-paper, which may be kept in contact with the liquor, is turned red. The number of graduations taken to effect this indicates the per centage of caustic alkali in the sample.

Another method of using test acid is by weight. The acid is made to such a strength as one or two grains by weight will exactly neutralize one grain of pure alkali. The vessel commonly used for this purpose is of the annexed form, but any convenient vessel will do. It is filled with the test acid, and the whole correctly weighed. The acid is then dropped from the small orifice into a weighed quantity of the carbonate until a neutral sulphate is produced, indicated as above by test-paper. The bottle with its contents is then again weighed; the loss of weight gives, by calculation, the quantity of real alkali in the sample. Say that every two grains of the test acid are equivalent to one grain of pure soda, and that twenty-five grains of soda-ash require twenty grains of acid to neutralize it, the real alkali present will be ten. Now 25 being the fourth of 100, the 10 is multiplied by 4, giving 40 as the per centage of the sample. This method of testing carbonated alkalis, provided the operator has a good balance, is more correct than that with the graduated tube, and equally simple.



Another very ready method, sometimes recommended, is to take a small flask and a test-tube that will go inside, and stand nearly straight. Fifty grains of the soda-ash are dissolved in a little water in the flask, and the tube, which is nearly filled with sulphuric acid, is carefully placed in the posi-

tion shown in the figure. A small tube is fitted into the mouth of the flask, and the whole is then carefully weighed; after which, by holding the flask a little on one side, the acid is poured from the tube into the soda solution. This should be done gradually that the effervescence may not be too violent. When all effervescence ceases, and the flask is well shaken, the cork is taken out, that the rest of chloride of calcium



the carbonic acid may freely escape; it is then put back, and the flask is again weighed: the loss of weight will of course indicate the loss of carbonic acid, and by this the quantity of soda present may be calculated. If the loss of weight be 10 grains, then as 22 the equivalent of carbonic acid, is to 31 that of soda, so is 10 to 14·09, which, being multiplied by 2, there being only 50 grains of soda used, gives 28·18 as the per centage of alkali in the sample. This method, however, is not much to be relied upon in testing the value of alkali.

There are a great many other modes of proceeding, all embracing the same principles as those detailed, and also a great variety of apparatus for the purpose, but it is needless to mention them.

It will be observed that the same principle applies to potash as to soda. In the process where the loss of carbonic acid is made the criterion, the difference is in the equivalents. The equivalent of potash being 47·2, the proportion becomes $22 : 47{\cdot}2 :: 10 + 2 : 21{\cdot}95 + 2 = 43{\cdot}9$ per cent. With the test acid process, there may be obtained an acid of such strength that one graduation will be equal to one grain of potash, which will be found in the same way as for soda, namely, by neutralizing a known weight of pure dry carbonate of potash.

The operation most frequently tried, is performed by neutralizing a given quantity of acid, which does for either soda or potash.—Prepare a little pure anhydrous carbonate of soda as described for the soda test; weigh 53 grains, which is an equivalent, and dissolve in water, then take dilute acid in the alkalimeter, and add it to the soda until it is perfectly neutral; mark the number of graduations it takes for this:

say it takes 30; then to every 30 of the acid add 70 of water, and thus we have a stock acid, of which 100 graduations is equal to an equivalent of any alkali. Thus,

100 graduations is equal to 32 grains caustic soda,
47·2 ..... potash,
17 ..... ammonia,
28 ..... lime.

To test by this method, take 100 graduations of the test acid, and weigh 100 grains of the alkali, and dissolve in 100 measures of water; add this solution to the acid till it is neutralized, and mark how many measures have been necessary to effect this; then the per centage of alkali is easily calculated. Say that 70 measures of the alkali solution have been necessary to neutralize the acid; if the alkali is soda, then the 70 grains of soda-ash will contain 32 grains of caustic soda; and the per centage is found by the following calculation:—

70 : 32 : : 100 : 45·7 per cent.

If the alkali is carbonate of potash, the 70 grains will contain 47·2 grains of caustic potash; and then the per centage is found by the proportion:—

70 : 47.2 : : 100 : 67.45 per cent.

For commercial salts, either of potash or soda, the mode of testing by neutralizing, is preferable to that which depends on calculating from the loss of carbonic acid, as there are sometimes portions of caustic alkali in the sample, which the carbonic acid process will not indicate.

It may also be observed that the acid test for soda, derived from a coincident in their equivalents, will serve equally well for potash, each graduation being 1 of caustic soda, and $1\frac{1}{2}$ of potash.

The process for making caustic soda from soda-ash, is the same as described for making caustic potash, namely, a quantity of ash is boiled, and, when boiling, slaked lime is added until a small portion taken out does not effervesce on adding an acid; but the equivalent of soda being less than that of potash, it requires more lime for a given weight.

The following table, constructed by Dr. Dalton, will be

found useful to the operative bleacher, showing the quantity of caustic soda in his solutions, indicated by the hydrometer:

Specific Gravity.	Alkali per cent.	Twaddell's Hydrometer.	Specific Gravity.	Alkali per cent	Twaddell's Hydrometer.
2·00	77·8	200	1·40	29·0	80
1·85	63·6	170	1·36	26·0	72
1·72	53·8	144	1·32	23·0	64
1·63	46·6	126	1·29	19·0	58
1·56	41·2	112	1·23	16·0	46
1·50	36·8	100	1·18	13·0	36
1·47	34·0	94	1·12	9·0	24
1·44	31·0	88	1·06	4·7	12

The remarks, (page 113,) in reference to the presence of sulphurets in potash-ley injuring the gold ornaments of light muslins, &c. are equally applicable here; and the same tests for ascertaining the presence of these impurities in potash may be employed to detect their presence in soda solutions. With respect to the solubility of soda—

100	parts water, at	62°	Fah. dissolve	41	parts of caustic soda.
100	,,	90°	,,	46	,,
100	,,	131°	,,	64	,,
100	,,	158°	,,	72	,,
100	,,	176°	,,	78	,,

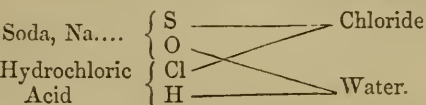
Cold water, saturated with soda, and brought to boil, attains a temperature of 266° Fah.

The salts of soda are in general the same in their chemical characters as the corresponding salts of potash, but they are not so generally used, on account, perhaps, of the disposition which almost all soda salts have to effloresce when exposed to the air.

Sulphate of Soda.—Soda, saturated with sulphuric acid, forms sulphate of soda, which crystallizes easily, and is known by the name of *Glauber Salts.* A dry and impure sulphate of soda is sold under the name of *salt cake;* it is obtained by heating common salt and sulphuric acid in making hydrochloric acid. It commonly contains about one-third of its weight of salt. A purer sort of salt cake is obtained by the makers of

nitric acid; in this process, the nitrate of soda is acted upon by sulphuric acid, and the product being valuable, considerable care is taken to have the nitrate decomposed. We have seen *salt cake*, from this source, containing as much as 98 per cent. of sulphate of soda.

Chloride of Sodium.—Hydrochloric acid, added to soda, forms hydrochlorate of soda (muriate of soda)—more properly, chloride of sodium, (common salt.) The action is as follows:



This salt is sometimes employed with nitric acid to make the *aqua regia* used for dissolving tin. It is often amusing to see the care taken to mix the acid and the soda to form what may be got so conveniently as common salt.

Nitrate of Soda.—Nitric acid, added to soda, forms nitrate of soda. This salt, as already stated, (page 52,) is found abundantly in nature, and is termed *cubic nitre*, from the shape of its crystals, and to distinguish it from nitrate of potash, (*nitre.*) When heated to redness, it is decomposed, and gives off much oxygen gas; it is often employed for this purpose, and for oxidizing metals in a fused state. It is also occasionally used for preparing some of the salts of tin for mordants, along with hydrochloric acid.

Borate of Soda.—Boracic acid with soda, forms borate of soda, (*borax* or *tinkal.*) This, as we have before noticed, (under Boron,) is also a natural product; it is used as a blowpipe re-agent for fluxing metals.

Phosphate of Soda.—Phosphoric acid, with soda, forms phosphate of soda, also a useful salt, as a test for the presence of magnesia in water solutions.

Soda, on account of its cheapness, has been substituted for potash in the manufacture of some of the salts most extensively used, such as ferrocyanides, chromates, alum, &c., but none of these modified salts have come into common use, not that they are less suitable in the dye-house, but for other reasons, which we need not here examine.

Lithium. (L 6·5.)

This is another alkaline metal, the oxide of which is termed Lithia. It has properties somewhat resembling those of soda and potash, and combines with acids as a base in the same manner as these other alkalis. It is, however, very rare, and only got in small quantities, from a mineral termed *Lepidolite*. It has not, as yet, been used in any process of manufacture, and has therefore no claim to our further consideration.

Soap.

In connection with the alkalis, it will be necessary to direct attention to *Soap*, an article of great importance in the dye-house. If we take a quantity of oil, and add to it some caustic alkali, a milk-white solution is obtained, which is found to be soluble in water. This solution, boiled down to a proper consistence and cooled, forms soap. All sorts of fats and oils are used in soap-making; they all contain certain acids, capable of combining with the alkali, and giving a detersive character to the compound. The soap made with soda is hard, that with potash soft; and the degree of hardness, in either case, varies according to the nature of the oil or fat employed. In manufacturing soap, care is taken to obtain a proper mixture of these fats and oils, so as to produce a soap of proper consistence. The following extract on this subject, from "*Normandy's Commercial Hand-book of Chemical Science*," is important:—

"Mottled soap has a marbled, or streaky appearance; that is to say, veins of a bluish or slate colour pervade its mass, which is white or whitish; the size and number of these veins depend on the more or less rapid cooling of the soap after it has been transferred from the copper to the frames. The blue or slate colour of these streaks is chiefly due to the presence of an alumino-ferrugenous soap interposed in the mass, and frequently, also, to that of sulphuret of iron, which is produced by the reaction of the alkaline sulphurets, contained in the soda-ley, upon the iron, derived from the iron, copper, and utensils employed in this manufacture, or, which even is, at times introduced purposely as sulphate of iron. The veins gra-

dually disappear from the surface to the centre, by keeping, by the oxydation of the sulphuret of iron. A well-manufactured mottled soap cannot contain more than 33, 34, or at most 36 per cent. of water. The addition of water causes the colour to subside, and a white soap is produced. This addition of water is made when the object is to give white soap; so that, with this additional quantity of water, white soap sometimes contains 55 per cent. It is therefore best to buy mottled soap in preference to yellow or white soap, the mottling being a sure criterion of genuineness, as the addition of water or other matters would soon destroy the mottling."—This quality of soap is not much known in Scotland: even the name is not used. "To yellow or white soap," says Mr. Normandy, "incredible quantities of water may be added. I have known 15 gallons of water added to a frame of already *fitted* soap, (10 cwt.), so that the soap, after this treatment, contained upwards of 60 per cent. of water. Common salt had been previously dissolved in the liquor."

"Besides being surcharged with water, soap is sometimes further adulterated with gelatine, made by boiling bones, sinews, hoofs, skins, fish, &c., in alkalis; also with dextrine, potato-starch, pumice-stone, silica, plaster of Paris, clay, salt, chalk, carbonate of soda, &c., &c.

Soft or *black soap*, is the most useful of all the soaps. It is made with fats or oils and a solution of potash, and always contains a great excess of alkali and much water; also chlorides, sulphates, and other impurities. Fish oil is also often employed in the making of this soap, which gives it a very disagreeable smell. Soft soap, which has a greenish colour, is best, although occasionally this colour is given to a very inferior article, by the addition of a little indigo.

The quantity of water in soap may be ascertained by taking 100 grains of the sample in thin parings, putting them into a water bath or oven, of which the heat does not exceed 212°, and allowing them to stand as long as they continue to lose weight, which is known by occasional weighing; the loss of weight indicates the water evaporated. In mottled soap, it should not exceed 35 per cent.; in the white and yellow soaps, it ought not to be more than 50 per cent.

The other impurities of soap may be detected by dissolving 100 grains in strong alcohol, and applying a gentle heat:

the soap is thus dissolved, and the impurities remain as precipitate. The best soap should not contain above one per cent. of matter insoluble in alcohol. Good soap may be known by its comparative transparency. When cut thin, the purer the soap is, the more translucent. Dry soap is also more transparent than wet.

The earths combine also with fats and form soaps, some of which are difficultly soluble in water, so that if there be oil or grease upon goods, and they are put into matters that form an insoluble or difficultly soluble soap, these spots will be so many white stains in the dyed goods; and when ordinary soap, made from fats, is put into water that has earthy matters or salts in it, these salts are decomposed by the alkali of the soap taking the acid, and greasy or insoluble soapy spots are produced. This is often experienced in washing with soap in hard water: these spots are sources of annoyance to the dyer.

When soap is dissolved in water, there should be no oily or fatty matters visible on the surface,—as this would indicate that too little alkali had been used in the manufacture of the soap. The following method of testing the quality of soaps is given by M. Dumas, in the *Chemie Appliquée aux Arts*, tome vi:—

"To determine the quantity of water, thin slices are cut from the edges and from the centre of the bars. A portion is then weighed, about 60 to 70 grains, and exposed to a current of air, heated at 212° F., or in an oil-bath, until it ceases to lose weight. The dry substance is then weighed; the difference between the first and last weighing will indicate the quantity of water evaporated. If it be a soft soap, it is weighed in a counterpoised shallow capsule. In good soap the amount of water varies from 30 to 45 per cent., in mottled and soft soaps, from 36 to 52 per cent.

"The purity of soap may be ascertained by treating it with hot alcohol; if the soap be white, and without admixture, the portion remaining undissolved is very minute, and a mottled soap of good quality does not leave more than about 1 per cent.

"If there should be a sensible amount of residue from white soap, or more than 1 per cent. from mottled soap, some accidental or fraudulent admixture may be suspected, silica,

alumina, gelatine, &c., the quantity and nature of which may be determined by analysis.

"The quantity of alkali contained in the soap is easily determined by means of the alkalimeter: a known quantity of the soap is dissolved in water, and tried by the test acid.

"There is no difficulty in ascertaining in the same assay the quantity of the fatty substance. For this purpose 150 grains of pure white wax, free from water, are added to the liquid after saturation with the test acid, and the whole heated to complete liquefaction; it is then allowed to cool, and when it has become solid, the cake of wax and fatty matter which have united is removed and washed, dried and weighed; the augmentation in weight beyond the 150 grains employed will give the weight of the fatty matter.

"The liquid decanted from the solidified wax may afterwards be tested to ascertain the purity of the base.

"The solution of the sulphate may also be evaporated, and by an examination of its crystalline form, or by means of chloride of platinum, it may be ascertained whether the base be soda or potash, or a mixture of the two.

"As to the nature of the fatty substance, it is ascertained, with more or less certainty, by saturating the solution of the soap with tartaric acid, collecting the fat acids, and taking their point of fusion. It is possible, at least, by this to prove the identity or the absence of identity with the sample in the soap supplied, for instance whether it is made from oil or tallow, &c. The odour developed by the fatty acids, at the moment of the decomposition of the soap by acids assisted by heat, will often indicate the nature of the fatty substance employed in its fabrication, or that at least of which the odour may prevail.

"The soap is proved to contain an excess of fatty matter not saponified, by separating the fatty acids by means of hydrochloric acid, washing with hot distilled water, then combining them with baryta, and thoroughly washing the new compound with boiling water. The non-saponified fatty matter is easily separated from the barytic soap, by treating the mass with boiling alcohol, which dissolves the fatty substance. We can, moreover, assure ourselves that it has no acid reaction on moistened litmus-paper, that it is fusible, and that it possesses the general characters of a neutral fatty substance."

Barium. (Ba 68·5.)

This is a metal having a silver-white lustre, and considerable ductility; it is four times heavier than water, rapidly oxidates when exposed to the air, forming Barytes, one of those substances termed earths, and which has strong alkaline properties. This earth, which was decomposed and its metallic basis discovered by Sir H. Davy in 1808, exists abundantly in nature, in combination with sulphuric acid, forming sulphate of barytes, (*heavy spar,*) and with carbonic acid forming carbonate of barytes. The artificial salts are generally prepared from the sulphate, which is ground fine, mixed with charcoal, and kept at a strong red heat in a crucible for about an hour. Sulphuret of barium is thus formed. This is now acted upon by nitric or hydrochloric acid, to form the nitrate or chloride, according as one acid or the other is used. These salts may also be obtained from the carbonate without previous heating, by merely digesting the mineral in the acid.

Chloride of Barium is a crystalline salt, of which 100 parts of cold water dissolve about 43 parts.

Nitrate of Barytes is also a crystalline salt, but not so soluble in water; 100 parts of cold water dissolve only about $8\frac{1}{2}$ parts of it. The affinity of barytes for sulphuric acid is very great; it takes it from every soluble substance, and forms with it an insoluble precipitate. Hence it is that barytes is pre-eminently the test for sulphuric acid.

The Acetate of Barytes is sometimes used to precipitate the sulphuric acid of alum, and form an acetate of alumina; but this use of the salt is not very extensive.

Strontium. (Sr 43·8.)

This is a metal very similar to Barium in appearance and properties. Its oxide is termed Strontia. It is another of the earths which has alkaline properties, and which occurs in nature in combination with carbonic and sulphuric acids, although not very abundantly. The artificial salts are prepared from the carbonate, by acting upon it with nitric or hydrochloric acid, by which is formed nitrate of strontia, or

chloride of strontium, both crystallizable salts. Its solutions precipitate sulphuric acid, but not so fully as the solutions of barytes. The salts of strontium are not used in manufactures, except indeed for fireworks: they have the property of communicating a red colour to flame.

Calcium. (Ca 20.)

This is a metal of which the oxide is Lime—one of the most widely diffused of all the earths, and also one of the most generally useful. It exists in nature as a carbonate and as a sulphate. Ordinary limestone, chalk, marble, &c. are carbonates; gypsum, plaster of Paris, &c. are sulphates.

Caustic Lime is obtained by heating the carbonate to redness—which is the ordinary process of lime-burning in a kiln. The carbonic acid is driven off, and caustic or burned lime remains. The caustic lime combines rapidly with one equivalent of water, and, becoming a hydrate, falls into a fine powder, commonly termed *slaked lime*. During this operation, much heat is evolved from the water as it passes from a fluid to a solid state in combining with the lime, and gives out its heat of fluidity.

Lime is soluble in water, producing lime-water, which has an alkaline reaction, much valued in the dye-house. It takes 78 gallons of water at 60° to dissolve one pound of lime; 97 gallons at 130°; and 127 gallons at 212°.

Thus we see that cold water dissolves more lime than hot water; so the practice of putting boiling water into lime, in order to get a strong solution, is erroneous; and when a boiler is filled with cold lime water, and brought to boil, as when oranges are to be raised, we see why there is always a quantity of powder deposited; for, as the hot water does not hold the same quantity of lime in solution as the cold, the surplus is deposited in fine crystalline grains. Lime water, exposed to the air, absorbs carbonic acid rapidly, forming a thin pelicle on the surface, which, falling down from time to time, the lime in the solution will ultimately be all deposited. Lime, in its caustic state, is extensively used in the dye-house, and we will hereafter have occasion to refer to it when describing the operations of the trade.

Lime combines with the acids, forming a series of salts of little practical use to the dyer. With hydrochloric acid it forms the chloride of calcium—a very deliquescent salt, which is sometimes on that account used in absorbing moisture from gases, &c. It is formed in the spontaneous decomposition of bleaching powder, which it makes damp. (See page 74.)

Sulphate of Lime is an insoluble substance, or nearly so, the acid and lime having a strong affinity for each other. This salt is formed in the common blue vat by the sulphate of iron. It is held in solution in very minute quantities in some spring waters.

Carbonate of Lime (*Limestone*) is soluble in water holding carbonic acid, probably forming a bicarbonate of lime.

The best test for the presence of lime is a solution of oxalate of ammonia, which gives with lime a white precipitate.

Magnesium. (Mg 12·2.)

This is a silver-white metal, ductile and hard, and oxidates rapidly when exposed to moist air and in water.

Magnesia.—The oxide is the well-known alkaline earth magnesia, which, having a low combining equivalent, is remarkable for its great power of saturating acids. Magnesia is abundant in nature, but it is found chiefly in the state of carbonate. There are immense beds of it in combination with lime, termed magnesian limestone. The carbonate is soluble in water, which contains free carbonic acid, and imparts to the water a slightly alkaline reaction. Magnesia combines with the acids, and forms with them a series of salts of considerable importance in several manufactures and in medicine, but they are not much used in dyeing. The salt principally used is the sulphate, (Epsom salt,) which exists in certain springs, and is easily prepared by saturating magnesia or carbonate of magnesia, with sulphuric acid, and evaporating the solution to crystallize the salt. Salts of magnesia in water are very bad for delicate colours. The best test for its presence is phosphate of soda, with which, after long stirring, it gives a white precipitate, even with very minute quantities.

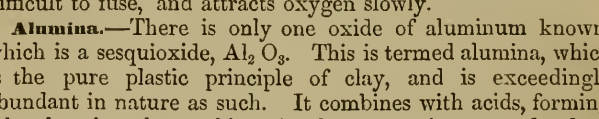
The five elements—Glucinum, Beryllium, Yttrium, Thorium, and Aluminum—have been termed the metals or bases of the *earths proper*, to distinguish them from the four elements

we have just been considering; these, from having alkaline properties, have been termed the *alkaline earths*. The first named four elements of the earths proper are very rare, and their characters have been studied by very few chemists; accordingly, little is known about them, and as no practical application has been made of any of them or their salts, we may dismiss them with this brief notice. But the fifth, namely, aluminum, is of vast importance, and consequently demands special attention.

Aluminum. (Al 13·7.)

The metal Aluminum is obtained as a greyish powder, very difficult to fuse, and attracts oxygen slowly.

Alumina.—There is only one oxide of aluminum known, which is a sesquioxide, Al_2O_3. This is termed alumina, which is the pure plastic principle of clay, and is exceedingly abundant in nature as such. It combines with acids, forming salts, but it only combines in the proportions stated: thus, by dissolving alumina in hydrochloric acid there is formed—



Alum.—Alumina is easily dissolved in sulphuric acid, forming the sulphate of alumina, which crystallizes with much difficulty; but this salt has a strong affinity for the sulphate of potash; so that when these two salts are mixed, or when a salt of potash is added to a strong solution of sulphate of alumina, they combine, and form common alum, which is easily crystallized. This is what chemists denominate a double salt, being composed of two sulphates—the sulphate of alumina, and the sulphate of potash. This salt has been known, and in general use among dyers, since the earliest accounts we have of their processes; but the true nature of its composition was not known till the present century. The alchymists knew that sulphuric acid was one of its constituents; and during the last century, it was discovered that the precipitate which falls when the acid is neutralized by an alkali, is a particular kind of earth which chemists called alumina, because of its being

obtained from alum. Amongst other peculiar properties of alumina, it has a strong attraction for organic matter, and withdraws it from solutions with such force, that if the purest water be not used when preparing it, the alumina is coloured; and when digested in solutions of vegetable colouring matters, provided the alumina be in sufficient quantity, it will carry down all the colouring matter from the liquid. By this means the pigments called lakes are formed; and it is this that makes it so valuable as a mordant. The fibre of cotton, when charged with this earth, attracts and retains colouring matters.

A very pure alum is obtained in the Roman States from *alum stone*, a mineral which is continually produced at the Solfatara, near Naples, and other volcanic districts, by the joint action of sulphurous acid and oxygen upon some of the felspathic rocks. This mineral contains an insoluble subsulphate of alumina, with sulphate of potash; but it is partially decomposed by heat; so that, for the preparation of alum, the mineral is simply heated, till sulphurous acid begins to escape, and is then treated with water, by which process a very pure and excellent alum is procured—much superior to that manufactured in this country. The alum of this country is manufactured from a mineral termed *alum shale*, a kind of clay slate, much impregnated with sulphuret of iron, which is essential to the manufacture. The general composition of this *alum ore*, as it is also called, is as follows, observing that the proportions of the several components vary according to the depth from which the ore is obtained: the table is therefore to be considered as giving only the average constitution:—

Sulphuret of iron,	26·5
Oxide of iron,	3·1
Alumina,	18·3
Silica,	10·5
Lime and magnesia,	3·0
Magnesia, potash, soda,	1·4
Coaly matter,	28·7
Water,	8·5
	100·0

The ore is built up in large heaps, with alternate layers of coal: these heaps are set on fire, and allowed to burn for several weeks. During this roasting process, a portion of the

sulphur is expelled, but the greater portion of it is converted first into sulphurous acid, by taking an equivalent of oxygen from the atmosphere, and finally into sulphuric acid, by taking a further proportion from the peroxide of iron contained in the mineral. The sulphuric acid does not, however, remain isolated, but combines with the iron and alumina, and forms sulphates with these oxides. The roasting being completed, the material of the heap is removed to large tanks or pits, into which water is allowed to flow, and which dissolves out the sulphates formed in the process. The solution is run into large tanks and evaporated, generally by causing a current of dry heated air to pass over the surface of the liquid. When the solution is in this way sufficiently concentrated, the sulphate of iron crystallizes, and is then removed; the sulphate of alumina, being very difficult to crystallize, remains in solution. All the iron having by this means been separated, the sulphate of alumina in solution is removed to other vessels, where there is added to it sulphate of potash, chloride of potassium, or other salts of potash. There is then formed the double salt of potash and alumina, which is *alum*, and which, after a few days standing, crystallizes, and is removed and packed for the market. There are some modifications of this process adopted by different makers, but this description exhibits the general practice of the manufacture, and illustrates sufficiently the principle upon which the practice is necessarily based.

Soda may be used in the operation instead of potash, which would give a soda alum, but, nowithstanding its being cheaper, there are practical objections to it. Soda alum is not so easily crystallized as common alum, and it effloresces when exposed to the air, which makes it take the appearance of a dry powder. Sulphate of ammonia may also be used instead of potash, giving an ammonia alum, which, however is expensive, and possesses no corresponding advantage over the ordinary article.

The following analysis, by Dr. Thomson, of the alum made in this country, will be useful:—

Potash,.....	9·86	Symbols.
Alumina,.....	11·09	$Al_2\ O_3\ 3\ SO_3 + KO\ SO_3 + 24\ HO.$
Sulphuric acid,	32·85	
Water, ...	46·20	
	100·00	

Thus every 100 lbs. of alum contain 46 lbs. of water. From the nature of the processes by which the alum is manufactured, we may expect it to contain small traces of sulphate of iron, a substance very delcterious to its use as a mordant or alterant. Iron may be detected by dissolving a little of the salt in distilled water, and adding a few drops of a solution of red prussiate of potash; or boiling a little, with the addition of a few drops of nitric acid, and adding yellow prussiate of potash. In both cases, a deep blue colour is immediately produced, if iron is present. The addition to a solution of alum of a few drops of gallic acid will give a black colour if iron be present. Or, if a little alum be put into a vessel, and caustic potash added till the solution is strongly alkaline, then the whole boiled, and set aside to cool and settle, the alumina will be dissolved, and if iron be present, it will subside to the bottom as a brownish precipitate. When the proportion of iron is considerable, it is better to reject the alum altogether, especially for bright light shades. We have often experienced bad effects from the use of such alum upon light shades of drab and fawn colours, when dyeing to a particular pattern. Having obtained the particular shade, on adding a little alum as *raising*, the iron, by combining with the sumach upon the cloth, produced a colour two or three shades darker than required; leaving no alternative but to take off the colour, and dye anew—a process much more difficult, and which produces a colour much less brilliant than the first.

Pure alum is soluble in water, and should give a colourless solution.

One gallon of water at		54°	Fahr. dissolves	1	lb. alum.
One	.....	86	.....	2	.....
One	.....	140	.....	3	.....
One	.....	158	.....	9	.....
One	.....	212	.....	35	.....

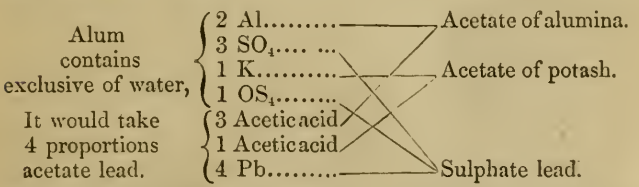
Alum forms but a weak mordant for cotton goods, owing to the strong attraction which the sulphuric acid has for the alumina; and in this state there are three proportions of acid to every two of alumina. But if we neutralize a portion of the acid, so that no more remains than is necessary to hold the alumina in solution, which, according to experiment, is not above a third of the acid contained in common alum, its proper-

ties as a mordant are greatly improved. That the amount of acid admits of being reduced, may be proved by taking a quantity of carbonate of soda, sufficient to neutralize the whole of the acid contained in a given portion of alum, dividing the soda solution into three equal portions, and adding gradually to the aluminous solution (stirring all the time) two of these portions: it will be found that, although the alumina is at first precipitated, by keeping up the agitation for some time, the precipitate again dissolves, forming an alum containing only a third of the acid of common alum. In this state, alum is a more powerful mordant for cotton, as the base is held more feebly by the sulphuric acid, and is readily detached by the superior affinity of the cloth to form a mordant; and thus prepared, it is perfectly pure: any iron formerly present is precipitated in the process. Alum in this state is known by the name of cubical or basic alum, from the form in which it crystallizes. We have already referred to Roman alum being superior to other alums. For a long time, the dyers considered this superiority to be wholly owing to its purity; but a chemical investigation shows it to be caused by the small quantity of acid it contains in comparison with ordinary alum.

Acetate of Alumina.—The most common, and we believe, the best method of using alumina as a mordant, is by substituting acetic acid for sulphuric acid as its solvent. The acetate of alumina has several advantages over the sulphate: 1st, the acetic acid is not so hurtful in its action upon the vegetable colouring matter; 2d, it holds the alumina with much less force than sulphuric acid, and consequently yields it much more freely to the cloth; and 3d, being volatile, a great portion of the acid flies off during the process of drying. When strong colours are wanted, and the mordant is of such a nature as will admit of being dried, it is better to dry the cloth from the mordant previous to dyeing. This last property of acetic acid is very convenient, as it frees the cloth from any superfluous acid which may have been in the mordant; besides, it has been found that during the drying by heat, the soluble acetate is converted into a less soluble subacetate. We may here put the dyer in mind that when goods containing volatile acids are drying, no other goods should be allowed to be in the same apartment, as the acid will be absorbed by them, and will affect almost

any colour that either has been or may be put upon them. Many unpleasant and also expensive consequences occur from the neglect of these precautions.

The acetate of alumina is easily prepared by mixing a solution of acetate of barytes, lime, or lead with alum. When any of these salts are added to alum, a double decomposition takes place; the sulphuric acid of the alum combines with the base of the salt which falls to the bottom, and the acetic acid unites with the alumina, forming acetate of alumina, which remains in solution mixed with sulphate of potash, which formed a constituent of the alum. The acetate of lead is the salt generally used for this purpose in the dye-house; the proportions of the lead and alum vary according to the nature of the colour to be dyed and the peculiar taste of the dyer, for the preparation of this substance is one of those operations which every one who practices it thinks he has the best method, but so far as we have had an opportunity of knowing, the superiority only existed in the mind of the individual, or rather in its being kept secret. In the proportions used for the preparation of this mordant there is never a sufficient quantity of acetate of lead to precipitate all the sulphuric acid in the alum. This crystallized acetate of lead has an equivalent of 190, and that of alum crystals of 475; but the alum, having 4 equivalents of sulphuric acid, would require 4 equivalents of acetic acid to take its place. Thus,



So that the equivalent of acetate of lead 190 must be multiplied by 4, giving 670, to be equal to 475 of alum. This is far from the proportions used, showing that the mordant is not a pure acetate of alumina, but a mixture of salts, probably of cubic alum with acetate of alumina and sulphate of potash.

The following method we have generally found to answer very well:—Into a boiler or pot put 20 lbs. of crystallized alum with about nine gallons water, and boil till the alum is

completely dissolved. In a separate vessel dissolve 20 lbs. of acetate of lead in about three gallons of boiling water. This is added to the alum while at a boiling heat, and well stirred. The sulphuric acid combines with the lead, forming an insoluble sulphate of lead, which falls to the bottom as a heavy white precipitate; the soluble part constitutes the mordant. The difference in the preparation of this mordant is in the proportion of lead varying from one half of the alum to equal weights. There is also added to the alum and lead a quantity of carbonate of soda varying from four to eight ounces to the five pounds of alum. This is added for the purpose of neutralizing a portion of the acid; but there are many dyers who will not use soda or any other alkaline substance when light bright shades are wanted, under the impression that the colour is much brighter without alkalis, but the difference of hue is hardly perceptible; some use lime; soda, however, is best. Without soda or some other alkaline substance, the mordant is not so effective. There are also some who object to the use of soda, as it throws down the alumina; but we have already noticed that a very little acid holds the alumina in solution; so that although soda, when added to the acetate of alumina, appears to precipitate the alumina, by a little agitation the precipitate is again dissolved, forming a mordant better adapted for strength of colour. From the following recipes, taken from a French work on dyeing, it will be observed, that the quantities of the aluminous mordants are similar both in England and France:—

60 gallons boiling water,
100 pounds alum,
100 pounds acetate of lead,
10 pounds crystallized soda,
} This mordant is best adapted for reds.

80 gallons boiling water,
100 pounds alum,
50 pounds acetate of lead,
6 pounds soda,
} This is best for bright yellows.

In addition to the above, Dr. Ure in his Dictionary of the Arts and Manufactures, article "Calico-Printing," gives another proportion:—

50 gallons boiling water.
100 pounds alum.
75 pounds acetate of lead.
10 pounds soda.

The following curious phenomenon was observed by Gay Lussac, viz., that the solution of a pure salt of the acetate of alumina may be boiled without decomposition; but if sulphate of potash, or any other neutral salt of an alkali be present, the solution becomes turbid when heated, and a basic salt precipitates, which dissolves again on cooling Now the acetate of alumina, prepared from the common alum, always contains sulphate of potash. If by the presence of this salt a portion of the acetate of alumina be thrown down when hot, and incorporated with the sulphate of lead, which falls in a very dense state, it may there be lost to the dyer. Whether this be so we know not, as we have not, since we knew of this phenomenon, had an opportunity of putting it to the test; but it would be advisable to stir the whole after becoming cold, that if any of this basic salt should be bound up with the precipitate, it might be set at liberty and dissolved; but it must be borne in mind, that if this be stirred when cold, it takes a long time to settle.

Nearly all the acetate of alumina used in dyeing, is prepared from pyroligneous acid, and is called by calico-printers *red liquor*, but by dyers *mordant*. No other substance, whatever be its nature, is distinguished as mordant. All other mordants have their technical names. The pyroligneous acid is one of the products of the destructive distillation of wood. The hard woods, such as oak, ash, birch, and beech, alone are used; they are put into large cast-iron cylinders, so constructed that a fire plays about them so as to keep them at a red heat, and having openings through which all volatile matter escapes by pipes, which lead into condensing vats. The products thus obtained consist principally of pyroligneous acid, mixed with a black tarry matter, having a very strong smell, from which the acid had its name, although it has been long since known that it is simply acetic acid (vinegar.) There is a great variety of other substances present, some of which have very singular properties, and some of the continental chemists suppose, they might be made available in dyeing. The products of the distillation of the wood are allowed to stand for some time, after which as much of the tarry matter as swims is skimmed off; the remainder is filtered, after which it is put into a boiler and heated a little, and lime added by degrees, till the acid is neutralized; then a quantity of lime is added in excess, and the

whole is made to boil; this throws up the tarry matter to the top, where it is taken off. When it is purified as much as it can be by this means, it is syphoned off into another boiler, and a quantity of alum is added; the acetate of lime, the sulphate of alumina and potash, mutually decompose each other; the sulphate of lime falls to the bottom; and the acetate of alumina remains in solution, which, when sent to the dyers, has sometimes a specific gravity of 1·90, (18 Twaddell) although it is often weaker, ranging from 12 to 18 Twaddell. It has a dark-brown colour, and a very strong pyromatic odour. When the acetic acid is wanted pure, it passes through a number of other processes which do not come within our province to describe in this place.

There is a considerable difference in the quality of red liquor, which the mere specific gravity does not indicate, as this can be brought up by the addition of foreign matters such as British gum, dextrine, and such like. A very simple method may be adopted to test the effective quality of the mordant:—Take a little of the liquor, and evaporate it to dryness, then burn the residue at a red heat until white in colour; put this into distilled water, which will dissolve out all but the alumina. Another way is by digesting a little of the red liquor in nitric acid, adding ammonia until the liquor smells of it, and then by filtering, the alumina is obtained upon the filter-paper. We will add four varieties here, to show the variableness in quality of the liquor as supplied to the dyer. The quantity given refers to the per centage in solution.

English red liquor—14° Twadd.	acetate of alumina	15·3
	sulphate of potash	·8
		16·1
Scotch, No. 1—13½° Twadd.	acetate of alumina	11·5
	sulphate of potash	2·3
		13·8
Scotch, No. 2— 14° Twadd.	acetate of alumina	14·
	sulphate of potash	1·2
		15·2
Scotch, No. 3—15° Twadd.	acetate of alumina	12·2
	sulphate of potash	2·6
		14·8

We have given these varieties to show how little reliance ought to be placed on the indications of the hydrometer. No. 3 is of a higher specific gravity than the English red liquor, but far inferior as a mordant. Again, such a mordant as No. 1 has a tendency to make light spots upon goods dyed green by fustic or bark, the alumina being the effective agent in the red liquor. The above is an ample illustration of the necessity of some better mode of testing than at present in use.

During the various applications of these aluminous mordants, and the manipulations attending them, many curious and interesting chemical phenomena are witnessed by the dyer, although his familiarity with them often prevents any particular remark; we shall instance one or two of those attendant upon the process of dyeing madder reds, by means of acetate of alumina. This process, however, is more immediately connected with calico-printing, while our particular object in this work is dyeing yarns and cloth to be finished as such. The cloth to be dyed is first thoroughly bleached and dried, it is then padded or soaked in acetate of alumina, about the specific gravity of 40°, (8 Twaddell,) and passed at full breadth through *nipping* rollers (squeezers). These are large rollers covered with cloth, which revolve one upon another. The pressure upon the piece, as it passes through for the purpose we are describing, ought to be such that it will dry in five minutes, passing over rollers in a stove heated to 160° Fah. Pieces mordanted with acetate of alumina, and dried at a great heat, are highly charged with electricity. If the hand be suddenly drawn along the piece, a complete shower of fire is observed, with a sharp cracking noise, at the same time a prickling sensation is felt. Whether this has any effect upon the mordant, in its immediately combining with other substances, we do not know; but cloth in this state is very ill to moisten: water runs off it as off a duck's wing, but as yet we offer no explanation. After being dried, the goods are passed through a dung bath, made up with about one part cow's dung to fifty parts water, at a heat of 130° Fahrenheit; from this they are well washed through the dash wheel. Into a boiler of cold water is put from one to three pounds of madder, according to the colour wanted, for every pound of cloth. The cloth is put in, and a fire is kindled under the boiler, and so regulated that it will boil in

two hours, during which the cloth is kept running over a *winch* or wheel, first the one direction and then the other, and kept spread as much as possible, so that the whole surface may be equally exposed to the dyeing operation. The boiler is kept at the boil from twenty to thirty minutes: this, with washing first through bran, and then water, completes the dyeing operation. If a white pattern be wanted upon these reds, the pattern is printed upon the goods with citric acid, (about 25° of Twaddell, thickened with pipe-clay and gum,) about twelve or twenty-four hours after being dried from the mordant. This decomposes the aluminous mordant upon these parts, so that no dye adheres to them afterwards. It is of the utmost consequence that the goods be thoroughly cooled previous to printing on the resist, otherwise there is danger of it not being successful.

Now, from a difference in the manipulation, or a little variation upon some of these processes, several curious changes take place upon the mordant. For example, were the pieces merely washed with water from the mordant, previous to printing on the resist acid, although the treatment be every way else the same, the discharge of the mordant is not effected; those parts upon which the citric acid is printed will be scarcely observable after the cloth is dyed, while in the other case they are perfectly white.

A somewhat similar result, in reference to the action of the discharge acid, takes place, if the heat of the stove in which the goods are dried from the mordant exceeds a certain temperature, or if dried upon steam rollers.* No acid, printed upon the cloth after this, will produce a white, except it be of a strength that will destroy the fabric of the goods; besides this, the colours afterwards dyed upon mordants heated in this manner are extremely bad, being heavy and dull.

Various opinions have been offered by practical men upon the probable cause of these changes: some suppose that by the excess of heat, the acetate of alumina is altogether decomposed, the acetic acid flying off, and the alumina left in the goods adhering with such an affinity, that it requires a stronger acid than the cloth will bear to disengage it; but from the similarity of the effects which take place, by merely washing

* Large metal cylinders, into which steam is admitted, and the cloth passed over the surface.

the piece from the mordant, this opinion is liable to objection, for the sub-acetate of alumina is not decomposed by washing with water; however, different causes may produce the same effects. If this opinion be correct, the circumstance of a bad colour resulting from the acetate being decomposed, will be a proof that it is not the alumina alone which constitutes a mordant, but its salt; in this case, it is the sub-acetate of alumina—the acetic acid being an essential ingredient to the dyeing process. This we are inclined to believe, for in those mordants, as we have already stated, where the acid can be separated by washing, the proper colour is not produced until some salt or acid be added to the colouring matter as an alterant. It is supposed by some writers that the dunging and washing extract the acid from the mordant, and leave the base upon the cloth. This, we conceive, to be an error; for although the part which dung acts in these processes is not well understood, yet, from the analysis of this substance, and the nature of the salts which are supposed to be useful in these operations, there is no probability of the aluminous salt being decomposed. One principal use of the dung bath is to combine with and carry off any loose or supernatant mordant which may be upon the cloth, not combined, and which might affect the colour, or more particularly the parts wanted to be white.

Alumina combines with all the acids, forming salts similar to those already described, and all difficult to crystallize, except as double salts—such as alum—which they form with other salts besides those named; but none of the others have been introduced into the dye-house.

Alumina, as an earth, is of great value in many other arts, as in pottery, brickmaking, &c. It also forms the bases of some of the finest precious stones: the sapphire and ruby, for example, are nearly pure alumina.

The salts of alumina, such as alum, act towards other salts and re-agents, as under:—

Potash .....White precipitate, which is redissolved in an excess of the precipitant.

Ammonia.....White precipitate, insoluble in an excess of the precipitant.

Carbonate of potash.....White precipitate, not soluble in an excess of the precipitant, but soluble in caustic potash.

Caustic soda, and its carbonate, act in the same way as caustic potash and its carbonate.

Carbonate of ammonia, and phosphate of soda, act in the same way as carbonate of potash.

All these precipitates are soluble in acids.

Oxalic acid.....No precipitate.

Yellow prussiate of potash...Precipitate, after standing for some time.

Red prussiate of potash.....No precipitate.

All these precipitates of alumina have a bulky and a kind of plastic appearance, easily recognized and distinguished.

When a substance containing alumina is heated to redness, especially before the blowpipe, and is touched with a solution of nitrate of cobalt, and then again heated, it takes a beautiful blue colour. In this way a very small portion of alumina may be detected in any solid substance; but when the substance is in solution, it must be detected by the reaction of some of the re-agents given above. It may also be noticed, that when operating to obtain a precipitate, it is necessary to be careful that only pure water is used for washing the precipitate. If the water is not pure, the precipitate will attract the impurity, especially if it consists of any organic matters, and thus become tinged, and assume an appearance as if iron were present.

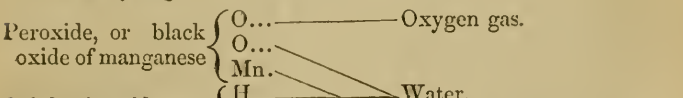
The next general division of chemical elements consists of the METALS PROPER. These are very numerous, but a great many of them are so rare as to have been seen by a very few chemists, and are only obtained in particular localities, consequently their properties have not been much investigated, and no practical applications have been made of them. Of these a very short description will suffice, so that our remarks may be more extended upon those which have a known practical value. The first of which is

MANGANESE. (Mn 27·6.)

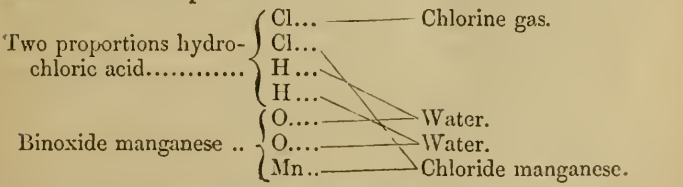
This metal is not found in nature in a separate state, but exists abundantly in combination with oxygen. From this circumstance it was long considered a species of earth,

like magnesia, and was consequently called *magnesia nigra*, but it was discovered to be the oxide of a metal in 1774 by Scheele and Gahn, and was then named manganese.

As a metal, it has a greyish-white lustre, resembling cast-iron; it is very difficult to fuse, and it combines with oxygen so quickly, that it cannot be kept in the open air. It passes into several states of oxidation. The one in which it generally exists in nature is the peroxide having 2 proportions of oxygen to 1 of metal = Mn O_2. When this oxide is heated at a low red heat, it loses a part of its oxygen, and passes into the state of sesquioxide = Mn_2 O_3. When heated to bright redness, it loses more oxygen, and becomes what is termed red oxide, or a mixture of the protoxide Mn O and of the sesquioxide Mn_2 O_3. The peroxide does not unite with either acids or alkalies. When boiled with sulphuric acid, one proportion of the oxygen is evolved, and the protoxide Mn O unites with the acid, and forms sulphate of manganese, which is used in dyeing.



When the peroxide is digested in hydrochloric acid, chlorine is evolved, and chloride of manganese formed. This is often done in houses for the purpose of fumigation. The reaction is thus expressed:—



The oxide of manganese is extensively used in the manufacture of bleaching powder, for obtaining the chlorine from common salt. (See page 71.)

Manganese combines with almost all the acids forming salts, which in their crystallized or dry state have less or more of a pinky hue. In making these salts from the per-

oxide, there is always oxygen liberated; they are therefore all what are termed salts of the protoxide. But by removing the acid, the protoxide soon combines with more oxygen, and becomes brown. It is this circumstance that has made it applicable in dyeing. In preparing any of the salts of manganese for dyeing purposes, care should be taken that the salt be free of iron, as that metal is deleterious. The sulphate of manganese may be freed from iron by exposing it to a red heat, then dissolving the residue in water. By this means the iron present is peroxidized, it is thus rendered insoluble, and consequently sinks to the bottom.

When cotton is passed through a solution of sulphate of manganese, and then through a weak solution of an alkali, the manganese oxide is left within the fibre, and by exposure becomes brown by attracting more oxygen. Or if the cloth be immediately passed through a solution of weak bleaching liquor, the protoxide is converted into peroxide without exposure. This is the method generally adopted; it gives a brown, which is very dull and heavy, but also very permanent.

Mineral Cameleon.—When peroxide of manganese is fused with carbonate or caustic potash, there is formed what has been long known as the *mineral cameleon.* When this is first put into water, it produces a deep green solution, but passes rapidly to a red by absorbing oxygen. This compound is not used in dyeing, but we think it contains properties worthy of examination. It illustrates very forcibly the effects of oxygen in changing the colours of substances, and the rapidity with which these changes take place; accordingly teaching the necessity of attending to every condition, no matter how apparently trifling, as often the merest trifle may be of the greatest consequence in a process.

The salts of manganese, in solution, are affected by the following re-agents:—

Potash	Brown precipitate.
Soda and ammonia	Brown precipitate.
Carbonates of potash and soda	Brown precipitate.
Yellow prussiate of potash	Dirty-green precipitate.
Red prussiate of potash	Brown precipitate.

Manganese is easily detected by this general property of

turning brown when exposed, and giving a brown with all the alkaline re-agents.

Iron. (Fe 28.)

This is one of the most useful, generally diffused, and abundant of the metals. There is almost no substance, whether organic or inorganic, quite free from iron. Its uses in the various arts and purposes of life are innumerable. The most common iron ores of this country are the clay iron-stones, of which there are several varieties, and in which the iron exists as a carbonate along with silica, alumina, carbon, and a little sulphur. The ore is first calcined at a red heat, which expels the carbonic acid and sulphur; it is then mixed up with limestone and coal, and put into a blast-furnace, and subjected to intense heat, the effect of which is, that the silica and alumina combine with the lime, and form a glass; the coal takes the oxygen from the iron, and passes off with it as carbonic acid; the metal meantime fuses, and, in consequence of its superior gravity, sinks to the bottom of the furnace, while the glass and scoriæ float above it, and are run off separately when the furnace is tapped.

Iron combines with oxygen in two proportions—

Protoxide of iron ..... Fe O.
Peroxide of iron ..... $Fe_2 O_3$.

Both of these oxides unite with acids, and form with them two classes of salts, distinguished from each other by affixing *pro* and *per* to their names. Both salts are extensively used in the dye-house.

M. Fremy gives the following statement of what he called a third oxide of iron, which he had obtained in combination:

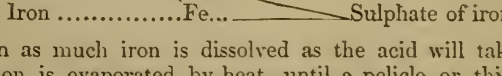
"This oxide is obtained by igniting a mixture of potash and peroxide of iron; a brown mass is the result, which, by digestion in water, gives a beautiful violet-red coloured solution. The compound is very soluble in water. A large quantity of water decomposes it in course of time. But it becomes insoluble in very alkaline water, forming a brown precipitate, which readily dissolves in pure water, and affords a fine purple-coloured solution. A temperature of 212°

dissolves it immediately; all organic substances decompose it; and hence it is impossible to filter the solution. It is impossible to isolate this compound, for when the red solution is treated by an acid, as soon as the potash is saturated, oxygen is disengaged, and peroxide of iron precipitated. If the acid be in excess, it dissolves the peroxide, and gives rise to the formation of a persalt of iron. It is stated to possess a powerful dyeing principle."

Protoxide of iron is very difficult to be obtained in an isolated state, on account of its great affinity for oxygen, which causes it to pass into the state of peroxide very rapidly. When an alkali is added to a protosalt of iron, the protoxide is precipitated as a hydrate of a grey colour, which, by exposure to the air, soon becomes peroxide of an ochery-red colour, as is seen almost daily in the dye-house during the dyeing of nankeen or buffs by a protosalt of iron or copperas.

The goods are dipped into the sulphate of iron solution, and then passed through lime water; the lime combines with the acid, and leaves the hydrated protoxide precipitated within or upon the fibre; the shade is then greenish, but a slight exposure peroxidizes the iron, and produces the nankeen or buff. This property of the protoxide of iron of passing into the peroxide, by its strong attraction for more oxygen, is beautifully applied in some of the operations of dyeing besides the one referred to, and which will be more fully described when treating of the blue vat.

Sulphate of Iron, (*green vitriol* or *copperas.*)—This salt is very easily prepared, merely by adding metallic iron to sulphuric acid, which has been diluted by 3 or 4 parts of water. The iron quickly dissolves, with rapid evolution of hydrogen gas. The reaction taking place may be thus represented:—



When as much iron is dissolved as the acid will take, the solution is evaporated by heat, until a pelicle or thin skin appears on the surface. It is then set aside in a cool place, and in a short time there is formed a quantity of green-coloured crystals of sulphate of iron. These crystals contain 7 proportions of water of crystallization, or in 100 parts

Sulphate of iron, $FeSO_4$	54·5
Water	45·5
	100·0

If these crystals are heated a little above the boiling point of water, to 238° Fah., they part with all this water except one proportion or about 10 per cent. The salt also loses its green colour, and becomes white. The crystals of sulphate of iron require the following quantities of water to dissolve them:—

1	gallon water at	50°	Fah. dissolves	6	lbs. crystals.
1	.....	59°	.....	7	.....
1	.....	75°	.....	$11\frac{1}{2}$	.....
1	.....	109°	.....	15	.....
1	.....	115°	.....	$22\frac{3}{4}$	.....
1	.....	140°	.....	$26\frac{1}{4}$	.....
1	.....	183°	.....	27	.....
1	.....	194°	.....	37	.....
1	... .	212°	.....	$33\frac{1}{4}$	.....

This table, which is of a similar character to tables of many other substances dissolving at a certain temperature, is interesting, and accounts for many of the circumstances occasionally observed in the dye-house—that sometimes the same stuff seems much more difficult to dissolve than at other times. It also shows why crystallization may occur much more rapidly at one time than at another. If we note the increase of heat and solubility, we will see how irregular they are:—

1st,	an increase of	9°	dissolves	1	lb. more than at	50°
2	.....	16°	.....	$4\frac{1}{2}$	.....	59°
3	.....	34°	.....	$3\frac{1}{2}$	.....	75°
4	.....	6°	.....	$7\frac{3}{4}$	.....	109°
5	.....	25°	.....	$3\frac{1}{2}$	.....	115°
6	.....	43°	.....	$0\frac{3}{4}$	.....	140°
7	.....	11°	.....	10	.....	183°
8	.....	18°	.....	$3\frac{1}{4}$	LESS than	194°

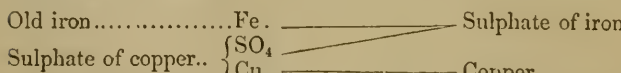
Ten gallons water, at 194°, will dissolve 100 lbs. more copperas than the same quantity of water only 11° colder—a fact quite sufficient to account for many of the phenomena which exist in the practical operations of the dye-house.

The sulphate of iron of commerce is not made by dissolving

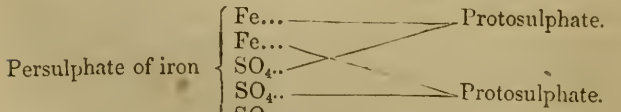
metallic iron in acid, which would be too expensive a process; but from the sulphuretted ores of iron, (iron pyrites.)

We have already, in treating of alum, given an account of the manufacture of a great quantity of the copperas of commerce; but there are numerous and extensive places for manufacturing this salt alone, where no alum is made. The operations are, however, nearly the same as those described for alum.

Iron pyrites is a bisulphuret of iron, $Fe\,S_2$; in 100 parts it has 52 of sulphur and 48 of iron. This compound, when obtained from the older geological formations, undergoes spontaneous decomposition by exposure to the air and moisture; the sulphur combines with the oxygen of the air, and forms sulphurous acid, which again, in the presence of water and oxide of iron, takes more oxygen, and becomes sulphuric acid, which in turn combines with the iron. Generally these pyrites are made into large heaps, and set on fire, in the same manner as the alum-shale is treated in the preparatory process of the alum manufacture. This roasting causes the rapid oxidation of the sulphur, and consequent formation of the sulphate of iron, which is all dissolved out, by passing water through the heaps, and collecting it into tanks. Owing to the excess of sulphur over the iron, there is generally in the solution an excess of acid, with also some persalt of iron, and often small quantities of copper, which would be deleterious. To get rid of this, a quantity of old iron is put into the solution, which takes up the excess of acid at the same time that it precipitates the copper from the solution. Thus,



It reduces all the persulphate of iron to the state of protosulphate:—Thus,



The solution is then evaporated to a proper density and crystallized. This method of adding old iron to produce the changes described, not being in all cases adopted, gives rise to some of the varieties of copperas found in the markets, concerning which there is much prejudice in the minds of dyers.

M. Dumas describes the variations to the formation of a double salt of the *proto* and *per* sulphate, during the decomposition of the pyrites. M. Bansdorff (*Records of General Science*) states, that there are three varieties of the protosulphate of iron; the first, greenish-blue, formed from an acid solution free from peroxide; the second, dirty-green, from a neutral solution without peroxide; and the last, emerald-green, from a solution impregnated with peroxide salt. This we know is consistent with experience,—that answering the description of his second variety being the best for general use; but the selection of this particular quality of copperas has led dyers into a fatal prejudice. Sulphate of iron crystallized from a neutral solution, if kept any time, assumes a rusty appearance by absorbing oxygen, and forming a film of peroxide of iron. Now, good copperas having generally this appearance, especially on the surface of the cask when opened, dyers pretty generally entertain the opinion that it is to this redness it owes its superior quality. This, we need hardly say, is an erroneous opinion, concerning which, Mr. Parkes mentions in his "Chemical Essays," that some unprincipled dealers take the advantage to sprinkle lime on the top of the cask to peroxidize the surface, and make the dyers believe that they have got a lot of excellent old copperas.

As copperas is generally judged of by the colour, the worst coloured copperas has sometimes a solution of common salt or of lime sprinkled upon it to give it a dark tint; but although this may deceive the eye, it does not improve its bad qualities.

Copperas, crystallized from solutions of sulphate of alumina, will also have an acid reaction when used for some of the purposes of the dye-house, such as the blue vat, and may be the origin of the light-green coloured copperas, by giving much more water of crystallization than the other. The difference of value between the light-green watery-coloured crystal and the dark-green, is, by experience, about 14 per cent. in favour

of the latter. The effects of this will be noticed more fully under the blue vat. But these results, we believe, to be the reason why a practical dyer, in an excellent treatise upon his trade, states that there is a bisulphate of iron, and warns the trade against its use.*

As this watery-looking blueish-green copperas, according to Bansdorff, crystallizes from an acid solution, it is probable that the extra proportion of acid which is found in it, is owing to a portion of the mother liquor being mechanically combined with the crystals, but not forming an essential ingredient in the composition of the salt. And if the salt has been crystallized from sulphate of alumina, the excess of acid will be more apparent.

The result of experience upon the relative value of the light-green watery-coloured copperas over the dark-green, or what are generally termed *new* and *old*, is as 21 to 24, or 100 lbs. of best old copperas is worth 114 lbs. of new light-green. In testing, there is always an excess of acid, but not in quantity anything like this difference. As the colour of the crystals of sulphate of iron depends upon the presence of water, may it not therefore be inferred that the difference of colour depends upon the proportion of water present in the crystals, which, if this be the case, will account for the different proportions of iron which we have often found in the same weight of the salt. It has been already noticed, that of the seven proportions of water which copperas contains, it loses six at 238°. We took 20 grains of each of the good and bad qualities of copperas, reduced them to coarse powder, and submitted them to a heat of between 305° and 400°, and taking the mean of several experiments, the bad copperas lost $1\frac{1}{2}$ grains more than the other, or $7\frac{1}{2}$ per cent., a result which agrees with the experience of the dyer. It being well known that copperas, being exposed to the air in a dry place, loses water.

English copperas is considered superior to Scotch. The former is mostly made from pyrites, while the latter is made from alum shale, and is therefore very liable to contain small portions of sulphate of alumina; and, being crystallized from a strong solution of the sulphate of a salt of another metal, has every chance of being inferior.

* Cooper's Treatise on Practical Dyeing.

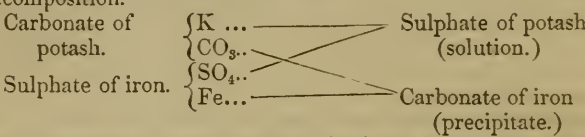
The presence of alumina may be detected by dissolving some of the salt in water, and boiling the solution, during which a few drops of nitric acid are added to peroxide the iron, which is known by the solution becoming a clear amber colour. Caustic potash is then added in considerable excess until the solution is alkaline, and the whole is then boiled for some time, and passed through a filter upon which the peroxide of iron is retained. The solution contains the alumina. The potash is neutralized by sulphuric acid, and on adding ammonia to this solution, if alumina be present, a flocculent white precipitate is obtained. Other tests for alumina are given under that element. If ammonia be added to the iron precipitate retained upon the filter, the solution passing through will become blue, if copper be present. It is best to test for the presence of copper separately: this is done by dissolving the copperas, as described, peroxidizing with acid, adding ammonia instead of potash, and filtering: the slightest trace of copper will tinge the solution blue. Or it may be detected by dissolving a little of the crystals, and putting into the solution a piece of clean polished iron, such as the blade of a knife: when if any copper be present it will be precipitated upon the iron in a metallic state. The presence of zinc may be detected in copperas, by taking the ammoniacal solution which has passed through the iron in testing for copper, and, if no copper be present, pass a stream of sulphuretted hydrogen gas through the solution; the zinc, if there be any present, will give a white precipitate. This metal is however very seldom found in copperas. The effects of the presence of these salts, in some of the operations where copperas is used, will be considered when treating of the blue vat. Magnesia is occasionally found in copperas, but its reactions are not deleterious.

Chloride of Iron.—Iron is easily dissolved in hydrochloric acid when treated in the same way as was described for dissolving the metal in sulphuric acid, and the product is chloride of iron.

This salt crystallizes in green coloured crystals, but with diffi-

culty. The crystals are very soluble in water, and pass rapidly into the *perstate*. For some purposes of dyeing this salt could be used equally with copperas., but for others, such as the blue vat, it would not do so well. Moreover, the expense of making it, precludes its extensive use in the arts.

Carbonate of Iron.—This salt, as we have already said, exists as an ore; but it is easily prepared, by adding to a solution of copperas, a solution of carbonate of potash or soda. It is a whitish green coloured precipitate, and is obtained by double decomposition.



This precipitate cannot be dried in the air without losing its carbonic acid and passing into the state of peroxide; but it is soluble in water impregnated with carbonic acid. This is the state in which iron is generally held in solution in spring waters.

Acetate of Iron.—Acetic acid or vinegar acts readily upon iron, dissolving it, and forming the acetate, which crystallizes in small green crystals, very rapidly acted upon by the air. This salt is much used in dyeing in the liquid state: it is known as iron liquor, and pyroliguite of iron, from its being prepared on the large scale with crude wood vinegar. The acetate of iron may be prepared by mixing together acetate of lead and protosulphate of iron. The sulphate of lead is formed and falls to the bottom; the acetate of iron remains in solution. The pyrolignite of iron is in general preferable. It is prepared by allowing iron to steep in pyroligneous acid (impure acetic acid) for several weeks. As this acid contains a quantity of pyrogenous oils and other impurities, it preserves the iron for a longer time in a state of protoxide than almost any other solvent available in the arts; hence the decided preference given to it by practical men. We shall often have occasion to refer to this subject, as it is one which is too much neglected, and which produces many serious evils. It may, however, be in the mean time observed, that pyrolignite of iron, used instead of copperas in dyeing black, gives a preferable shade of colour.

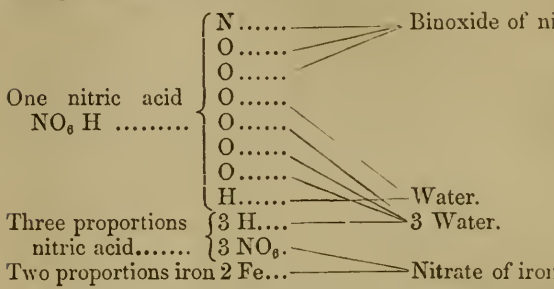
The value of this solution may be taken by evaporating a known weight to dryness, and burning the residue until all organic matters are consumed, when there remains only the iron as a peroxide: every forty grains of the peroxide will be equal to ninety-six of the acetate of iron in the solution. The operation is very simple, and the per centage of acetate of iron in the solution known. The average of good iron liquor ranges about 13·5 per cent. of pure protoacetate of iron, the specific gravity being about 1·085 = 17° Twaddell. The state of oxidation in which a metal exists, when used as a mordant, ought to be strictly attended to.

Iron combines in the protostate with oxalic acid, tartaric acid, and indeed with all the acids, but these salts possess no peculiar advantages over those before described to warrant any extra expense in preparing them.

Persulphate of Iron.—Persalts of iron are also extensively used in the dye-house. The persulphate of iron may be easily prepared, by boiling a solution of copperas, to which a few drops of sulphuric acid have been added, and, while boiling, adding a very small portion of nitric acid, or any nitrate: red fumes are given off, and the solution becomes of a beautiful amber colour. It is then in the state of a persalt. Chlorate of potash may be used instead of nitric acid or nitrates. The persulphate of iron might be advantageously used for many operations, and be cheaper than the nitrate of iron.

Nitrate of Iron.—This is the persalt of iron generally used in the dye-house. It is made by putting clean iron into nitric acid, by which it is very quickly dissolved. The iron ought to be added as long as the acid continues to dissolve it; but cautiously, otherwise the action will be so violent as to cause it to boil over. When engaged in this process, care ought to be taken not to breathe any of the fumes which come off, as they are very destructive to health. The reaction which takes place between the acid and the iron may be expressed as in the table below—which we introduce by remarking, that in dissolving iron in sulphuric or hydrochloric acid, there is merely a substitution of the iron for the hydrogen (see page 32); but with nitric acid a different range of affinities takes place: the elements of the acid are not held together so powerfully as those of sulphuric acid; so that one

proportion of the nitric acid is broken up, producing the following arrangement:—

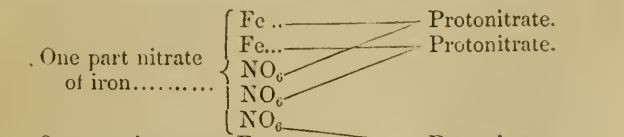


The binoxide of nitrogen is the gas passing off; but it instantly combines with more oxygen, and forms peroxide of nitrogen.

The nitrate of iron alone dyes a buff or nankeen colour, which is probably the easiest dyed of any of the colours, and is, at the same time, very permanent. The process only requires that a little of this salt be put into water, and that the goods be immersed in the solution for a few minutes, then washed in clean water and dried. Passing them through a weak soap solution softens the goods, and gives clearness to the tint. But the particular use of this salt is for Prussian blue. The goods are first dyed buff by the salt of iron, then thoroughly washed, and put into a very dilute solution of ferroprussiate of potash, made acid by a few drops of sulphuric acid; they are washed from this in clean water, to which a little alum has been added. (This is only for light blues on cloth: but for dark blues, and for yarn, the proper methods will be given hereafter.) We have known many attempts made to substitute copperas for nitrate of iron in dyeing Prussian blue, but need hardly say they were unsuccessful. A very little knowledge of the nature of these salts would have told the experimenters that protosalts of iron give only a greyish colour with yellow prussiate of potash; but, with red prussiate of potash, copperas is a better mordant than nitrate of iron, as the red prussiate gives a dark blue with the protosalts, and only a greenish grey with the persalts of iron.

The preparation of nitrate of iron (*killing* iron) is apparently one of the most simple operations of the dye-house, as all that is required is to place metallic iron into nitric acid; but the practical dyer often experiences difficulties which he cannot account for, and which alter materially his shades and colours. Sometimes, as we have already noticed, the iron seems not to be acted upon; at another time the action is so rapid that there is a difficulty in preventing the liquid boiling over. When the acid is a little diluted, and the iron is added in small pieces, the action is violent, and there is formed a brown turbid clay-looking solution. Colours dyed by the iron in this state are never brilliant. We have seen solutions of this sort diluted largely with water, the brown mass allowed to settle, and the clear only used, but this is tedious, and not good after all. The best means of improving this mordant is to remove all metallic iron, add a little nitric acid, and apply heat.

When the nitric acid is not diluted, and the iron dissolves freely, and when the acid is saturated with iron, if the remaining metallic iron is not removed, it continues to dissolve by the reaction of the nitrate of iron upon it thus—



This protonitrate rapidly imbibes oxygen, passes into the pernitrate, and, in so doing, liberates a portion of oxide of iron which collects at the bottom of the vessel, and accumulates so rapidly that the iron solution is soon converted into a brown paste. This can be avoided by taking out the iron when the acid is saturated, and before this deposit begins. The addition of a little acid and heat re-dissolve this oxide; or a little sulphuric or hydrochloric acid also dissolves it, and with it forms an excellent mordant.

A still more remarkable circumstance often occurs: the iron being placed in the acid, and action going on favourably, after a few hours, particularly if the weather be cold, the solution is observed to have a greenish yellow colour, and the vessel is

found to be half filled with crystals of a light yellow tint. Although these crystals, when dissolved in water, or the solution above the crystals, may be used for dyeing, they give varieties of quality from the usual iron solution, which often seriously destroy the method of the dye-house. The true nature of the crystals is not well understood, and it is difficult to get at their examination, as they are very deliquescent, dissolve easily in water, and even in their own water of crystallization, by a slight elevation of temperature above summer heat. When put upon blotting paper they are decomposed, and the paper imbibes much of the iron. We long thought that they were caused by the formation of ammonia in dissolving the iron, but experiments have failed to show the slightest trace of ammonia. The analysis of these crystals, by J. M. Ordway, gave 3 nitric acid, 1 peroxide iron, and 18 water = 3 NO_5 + Fe_2 O_3 + 18 HO. The same author has examined nitrates of iron of different qualities, and states that nitric acid combines definitely with various proportions of peroxide of iron and water, forming what he terms basic nitrates, varying from 3 acid, and 1 peroxide iron, to 3 acid, and 2, 3, 6, 8, 12, 15, 18, and 24 peroxide of iron, with various definite quantities of water, giving an interest to this salt of the highest sort, and amply accounting for the great difference experienced in its use for dyeing; and also for the ease with which peroxide of iron is fixed upon the fabric when put into this salt: the basic salt being decomposed, and a portion of the oxide of iron left upon or within the fibre. There are many other phenomena observed in working with these salts, which we will yet have occasion to notice.

Any other persalt of iron may be formed by adding ammonia, soda, or potash, to the nitrate of iron solution, so long as a precipitate is formed, washing the precipitate, by repeatedly filling the vessel which contains it with water, allowing it to settle, and decanting off the clear, then adding to the precipitate the acid of which the salt is wanted. The application of heat assists the solution of the precipitate in the acid. By these means per acetate, per oxalate, per tartrate, &c., may be obtained either for practical use or experiments.

The following is the reaction of different substances upon the *pro* and *per* salts of iron.

Protosalts.—Potash, soda, and ammonia give at first a grey-

white precipitate, passing into green, then bluish, and which, by exposure, finally becomes brown.

Carbonates of these alkalis produce precipitates, which pass through the same changes as the alkalis themselves.

Yellow prussiate of potash....A grey-white precipitate, which, by exposure, becomes blue.
Red prussiate of potash .....An immediate dark-blue precipitate.
Solution of galls.....A blue-black, not changed by standing.

Per Salts of Iron.—Alkalis, and carbonates of the alkalis, all produce dark-brown precipitates.

Yellow prussiate of potash....An immediate dark-blue precipitate.
Red prussiate of potash.....No precipitate, but the solution becomes green.
Solution of galls.....Black, passing to brown by standing.

The difference between the action of red and yellow prussiates will be remarked.

Cobalt. (Co 29·5.)

Cobalt generally occurs in nature in combination with arsenic and sulphur, and accompanied by other metals. The mineral in which it occurs was long known to miners, and was called by them *kobalds*, or *evil spirit of the mines*, because its appearance often deceived them by giving a favourable impression of mines which turned out erroneous, the cobalt being taken for something else. Its distinct character as a metal was discovered in 1733. Its oxide has long been extensively used for giving a blue colour to glass and porcelain. As a metal it is brittle, of a reddish grey colour, and little more flexible than iron. Its has two oxides similar to iron.

Protoxide,..... Co O
Peroxide,..... $Co_2 O_3$

But there is no persalt of cobalt known equivalent to the peroxide.

Cobalt is easily dissolved in either hydrochloric or nitric

acids, and forms pink-coloured solutions which produce crystals of a beautiful red colour. Solutions of these salts form sympathetic inks. By writing upon clean paper with one of these solutions, the writing is invisible when dry; but by heating the paper before a fire, the writing becomes blue, and disappears again on cooling. If the heat applied be too strong, the writing becomes black and permanent, a significant fact to the dyer. Cobalt does not dissolve easily in sulphuric acid; but a sulphate may be prepared by adding sulphuric acid to the oxide or carbonate, which is formed by adding a carbonate or caustic alkali to the nitrate or hydrochlorate of cobalt. The sulphate salt has also a pink colour, but is not so generally used as the others. Salts of any of the acids may be prepared by dissolving the oxide or carbonate. They are all affected by heat in the manner described.

Some of these salts might be very usefully employed in dyeing, were they obtained at a sufficiently low cost; but they are progressively becoming cheaper, and may therefore ere long be made available in the dye-house.

A preparation of cobalt is used in bleaching, as *smalt blue*. It is a compound of oxide of cobalt and alumina, prepared by mixing a solution of salt of cobalt and alum, and precipitating them together by an alkaline carbonate, as carbonate of soda, drying the precipitate, and subjecting it to a red heat. The process gives a beautiful blue mass, which is ground to an impalpable powder, and mixed commonly with some carbonate of lime (chalk). Salts of cobalt give the following reactions with other substances:—

Potash, soda, and ammonia...	A green colour by a little exposure.
Carbonates of the alkalis.....	Reddish precipitates, which become blue by boiling.
Phosphate of soda.....	Blue precipitate.
Yellow prussiate of potash	Green precipitate, which changes to grey.
Red prussiate of potash.....	Reddish-brown precipitate.
Sulphurets of the alkalis.....	Black precipitates.

The slightest trace of cobalt may be detected by the blowpipe, by fusing a little borax, and adding a little of the substance suspected to contain cobalt: if it be really present, it communicates to the borax a blue colour, more or less intense.

Nickel. (Ni 29·6.)

Nickel occurs in nature combined with arsenic, iron, cobalt, and sulphur. It was discovered in 1751. Isolated, it is a silver-white metal, ductile and malleable, and requires a heat nearly equal to that of iron to melt it. It is much used in the arts for alloying with other metals. It is the principal constituent of German silver. Nickel combines with oxygen in two proportions.

Protoxide..... Ni O.
Peroxide ..... $Ni_2 O_3$.

There are no per salts of nickel equivalent to the peroxide known.

Sulphate of Nickel.—Sulphuric acid dissolves nickel with difficulty. When the sulphate is required, the acid is applied to the carbonate or oxide of the metal; in this state it is easily dissolved, and forms a beautiful green-coloured solution.

Chloride of Nickel.—Hydrochloric acid when dilute, dissolves nickel, and forms a chloride; the solution is emerald green.

Nitrate of Nickel.—Nitric acid dissolves nickel easily, and may be called its true solvent: the product is the nitrate, of which the solution is also emerald green. All these salts crystallize.

Carbonate of Nickel.—This salt is prepared by precipitating the nitrate by a carbonated alkali, as carbonate of soda or potash. It is a greenish coloured precipitate. The common means of preparing the salts of nickel is by dissolving in nitric acid, then precipitating and washing the precipitate; by adding the required acid the precipitate is dissolved. The acetate, or oxalate, or any of the other salts, may easily be prepared in this way. The use of any of these salts in the dye-house is very limited. Their solutions are precipitated as follows:—

Alkalis.....An apple-green precipitate of hydrated oxide, insoluble in excess.
Ammonia, in excess.....Blue solution.
Carbonate of the alkalis .....Green precipitate.
Yellow prussiate of potash...Greenish-white precipitate.
Red prussiate of potash .....Yellow-green precipitate.
Solution of galls .....No precipitate.
Phosphate of soda .....White precipitate.
Sulphuret of the alkalis .....Black precipitate.

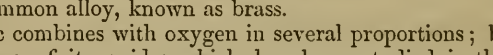
Zinc. (Zn 32·6.)

Zinc was discovered in the sixteenth century. It is very abundant in nature, in combination with sulphur, and with carbonic acid. With the former, it is the ore called *blende*, or *black jack;* with the latter, it is *calamine.* Zinc is a white metal with a shade of blue, brittle, and of a crystalline structure. When heated from the boiling point of water to 300°, it is ductile, and admits of being rolled into sheets, in which state it has become a most useful metal in the arts. At a red heat it rises into vapour, and takes fire in air, burning with a white flame. It is much used along with copper for making the common alloy, known as brass.

Zinc combines with oxygen in several proportions; but the only one of its oxides which has been studied is the protoxide = Zn O. The salts found are the protosalts, equivalent to this oxide.

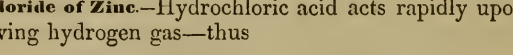
Protoxide of zinc may be obtained either by burning the metal, or by precipitating it by an alkali from its acid solutions. It forms a white powder, which is soluble in all the caustic alkalis.

Chloride of Zinc.—Hydrochloric acid acts rapidly upon zinc, evolving hydrogen gas—thus



It crystallizes in white crystals, which are very deliquescent, and often used on account of this property for keeping substances damp. It is even said to be employed by tobacconists for keeping snuff and tobacco moist, a dangerous and most reprehensible practice, if true. It is now very extensively used for soldering instead of rosin.

Sulphate of Zinc.—This salt is easily prepared by acting upon zinc with sulphuric acid slightly diluted: the action is



It crystallizes in white-coloured crystals, which contain seven proportions of water of crystallization, and dissolve in two

and a-half times their weight of cold water. It is known in commerce as *white vitriol*, *white copperas*, and is produced in great quantities in the soldering of platinum vessels. Articles of this kind are soldered by the flame of the oxyhydrogen blowpipe, for which the hydrogen required, is prepared by zinc and sulphuric acid, and thus the sulphate becomes a product.

Nitrate of Zinc.—This salt is easily prepared by acting upon the metal with nitric acid; it is a crystalline salt, very deliquescent, but not much used.

Acetates, oxalates, and salts of such milder acids, may be prepared either by digesting the metal in the acids, or by acting upon the oxide or carbonate found as a precipitate. The salts of zinc are not much used in the dye-house; the precipitates formed from them are nearly all white; but the sulphate is used in several operations, where its elements may act an important part without affecting the tint, as in the operations of dyeing *chrome yellows*, &c. It is also used by calico-printers in some of the operations of discharging.

The salts of zinc act towards other substances as follows:—

Potash, soda, and ammonia...	White precipitate, easily dissolved in an excess of the alkali.
Carbonates of the alkalis	White precipitate, not soluble in excess, but soluble in caustic alkalis.
Yellow prussiate of potash.....	White precipitate.
Red prussiate of potash.....	Yellowish-red precipitate; fades in the air.
Solution of galls.....	No precipitate.
Sulphurets of alkalis	White precipitate.
Chromic acid.....	A purple-brown precipitate.

Cadmium. (Cd 56.)

This metal was discovered in 1818; it is very rare, found only in small quantities, and sometimes combined with zinc. The metal somewhat resembles tin in colour; it is also soft and flexible, and makes a crackling noise when bent. It melts easily, and passes off as a gas at a heat of about 600°. It combines with oxygen in equal proportions, forming the

protoxide, (Cd O,) which has an orange colour, and is easily obtained by burning the metal in air, or by precipitation from acid solution by a caustic alkali. Prepared in this way, it is a white hydrate, and has one proportion of water combined with it. This oxide is soluble in ammonia, but not in soda or potash.

Cadmium is acted upon like zinc, both by sulphuric and hydrochloric acids; and forms crystallizable salts. Nitric acid acts readily upon the metal to form the nitrate, which is crystallized with difficulty. All these salts give white-coloured crystals. The salts of the milder acids, as the acetate, the oxalate, &c., may be obtained by dissolving the precipitated oxide or carbonate in the particular acid.

Potash and soda, and their carbonates, give white precipitates, not soluble in excess.

Ammonia—white precipitate, soluble in excess. (The oxide and carbonate, precipitated by the fixed alkalis, are all soluble in ammonia.)

Yellow prussiate of potash...White precipitate.
Red prussiate of potash.....Yellow precipitate.
Solution of galls.....No precipitate.
Sulphurets of the alkalis.....Beautiful yellow precipitate.

Copper. (Cu 31·7.)

This is a very abundant and useful metal, and was known in the earliest times. It is found in nature in great quantities, in combination with sulphur, oxygen, and carbonic acid; and is separated from these combinations by various processes of roasting and fusing. Copper is of a red colour; is very malleable and ductile, and only inferior to iron in tenacity. It requires a heat of about 1900° to fuse it. It combines with oxygen in two proportions, namely—

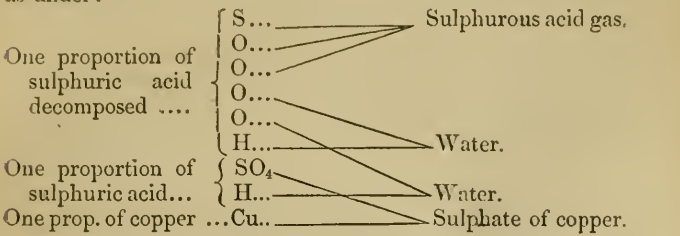
Suboxide or dinoxide.....Cu_2 0.
Protoxide .....Cu 0.

The suboxide is of a reddish brown colour, which is not changed by the air. If acted upon by dilute acids, a proto-salt is formed, and in strong hydrochloric acid there is formed a subchloride = Cu_2 Cl. This is a greenish or nearly colour-

less solution, which undergoes decomposition by dilution; and if precipitated by an alkali, oxygen is absorbed, and protoxide is formed. If a portion of suboxide be put into a stoppered bottle with ammonia, it is dissolved, and the solution is colourless at first, but by admitting air it is oxidised, and the solution becomes blue.

Protoxide of Copper is black, and is formed upon the surface of metallic copper when brought to a red heat and exposed to the air; or it may be obtained by exposing the carbonate, acetate, or nitrate, to a red heat. Alkalis added to solutions of copper precipitate the oxide as a hydrate of a blue colour, which becomes black by boiling. Oxide of copper dissolves readily in ammonia, and gives a deep blue-coloured solution.

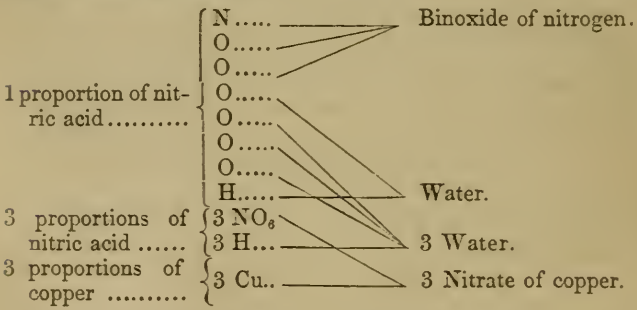
Copper combines with nearly all the acids, and the salts produced are generally blue or green. Sulphuric acid, when cold, does not dissolve copper, but at a boiling heat it acts upon it readily, a portion of the acid suffering decomposition, as under:—



Sulphate of Copper yields deep blue crystals, containing five proportions of water, four of which are given off by heating the crystals to 212°, at which temperature they become white. They are soluble in four times their weight of cold water, and in twice their weight of boiling water. The salt is prepared on the large scale, in the same manner as the sulphate of iron; that is, from the sulphurets of the metal. Great quantities of it are produced by the metal workers in Birmingham and elsewhere, in their cleaning and bronzing operations, which are effected by the action of acids upon copper or its alloys. As obtained in commerce, it is very impure, and is often contaminated with iron, a very injurious ingredient for

most of the purposes to which this salt is applied in the dye-house. This impurity can be detected by dissolving a little of the salt in pure water, and adding ammonia in excess, on filtering through paper, and washing the filter, the iron will be obtained as a brown precipitate of peroxide. If the salt contains much iron, it ought to be rejected. Zinc is often present, but it has no deleterious effects further than in lessening the value of the salt. Sulphate of copper is known in commerce and in the dye-house as *blue vitriol*, *Roman vitriol*, and *blue-stone*.

Nitrate of Copper.—Nitric acid dissolves copper easily, forming the nitrate; the action is similar to that by which the nitrate of iron is produced.



Nitrate of copper crystallizes in deep blue crystals, which deliquesce in the air, and are accordingly very soluble in water. The salt acts rapidly upon tin; if a small crystal be crushed, slightly moistened, and wrapped in tinfoil, combustion takes place by the rapid oxidation of the tin. The salts of copper are very useful for oxidizing vegetable matters in solution, and are often used for that purpose in the dye-house.

Chloride of Copper is made by digesting oxide of copper in hydrochloric acid, by which a double decomposition takes place as follows:—

The solution of this salt is green, but it crystallizes from this solution in blue-coloured crystals.

Acetate of Copper (*verdigris*) is prepared by exposing sheets of copper to the action of acetic acid (*vinegar*,) sometimes in solution, but more commonly in vapour. The salt is obtained in beautiful dark-green crystals; in this state it is a subacetate, having *one* acetic acid to *two* of copper. Acetic acid combines with copper in various proportions, and the verdigris of commerce is often composed of several salts, not by adulteration, but formed in the process of manufacture.

Oxalate of Copper is of a light-green colour, and is prepared by digesting oxide of copper in oxalic acid.

Arseniate and the Arsenite of Copper are salts of a light-green colour, formed during the dyeing of arsenic greens —*blue-stone sages* or *Scheele's green*—for which the goods are passed through strong solutions of arsenic and copper, and alkalis. That these greens are still dyed argues little for mercantile morality. This process of dyeing is dangerous, and the winding of the yarns, and other operations that follow, are more so, and produce much serious mischief to the operatives.

Copper salts produce the following reactions:—

Potash and soda	Greenish-blue precipitates, become black with boiling.
Ammonia	Deep-blue liquid.
Carbonate of alkalis	Green precipitate.
Yellow prussiate of potash	Dark-brown precipitate.
Red prussiate of potash	Yellow-green precipitate.
Solution of galls	Brown precipitate.
Sulphurets of alkalis	Black precipitates.

Lead. (Pb 103·7.)

This metal exists abundantly in nature, mostly in combination with sulphur, from which it is separated by exposing the ore to a gentle heat; the sulphur becomes oxidized, and passes off as sulphurous acid, and the lead melts, and runs off by a channel prepared for it.

Lead has a blueish-grey colour, is soft, and very malleable;

it does not oxidate readily in the air, except at the water line, when it is partially immersed in that fluid, and more rapidly still when the water is soft and pure. Hence lead vessels should not be used to hold water for domestic use, as the oxides of lead are all very poisonous.

Lead combines with oxygen in various proportions.

Suboxide of Lead is the greyish-blue crust, formed upon the surface of lead exposed to the air, and consists of two equivalents of lead and one of oxygen, $Pb_2 O$. It may be prepared artificially, by burning oxalate of lead in a retort; the suboxide remains as a dark-grey powder.

Protoxide of Lead consists of lead and oxygen in equal proportions, = Pb O. It may be obtained by exposing metallic lead at a red heat to a current of air; the oxygen of the air combines with the lead, and forms with it a semi-fluid mass. As it cools, it crystallizes in concretions of a greenish-yellow colour. It is obtained on the large scale by cupellation—a process of fusion to which lead is subjected in the process of extracting the small admixture of silver it commonly contains. The process is conducted as follows:—A quantity of lead is put upon a flat vessel made of bone ashes (*burned bones*) placed in a furnace; when the lead is melted, a strong current of air is blown upon the surface, which rapidly oxidates the metal; at the same time, the force of the current blows the oxide off, which runs over the side of the vessel like water. The silver, not being capable of oxidation, by this means is ultimately left pure upon the bottom of the vessel. Lead is continually added, until the silver remaining nearly fills this bone-ash vessel, which is technically termed a cupel.

When the protoxide of lead is kept for some time, it falls into a brick-red scaly crystalline powder, known in commerce as litharge. This is the principal oxide from which the salts of lead are prepared for the dye-house; but it is generally to some extent contaminated with iron, copper, and red lead, and is also subject to much intentional adulteration. Litharge, of good quality, possesses a crystalline lustre, and is completely soluble by digestion in nitric acid. The amount of adulteration, if it be brick-dust, may thus be ascertained, as it remains insoluble, and by adding ammonia to the solution, the lead is precipitated; if iron be present, the precipitate will have a brown colour; if copper, the solution will be blue, but none of these

are deleterious to the dye. The protoxide of lead is also obtained by adding a caustic alkali to a solution of a salt of lead; the oxide is precipitated as a white powder, soluble in an excess of caustic alkali, and also in solutions of the alkaline earths, as lime, with which it forms compounds more or less soluble.

Peroxide of Lead consists of two equivalents of oxygen and one of lead = Pb O_2. It may be obtained by digesting litharge in a boiling solution of chloride of lime, (*bleaching powder.*) It is a powder of a dark-brown colour, and is not used for preparing any salts of lead.

What is termed the fourth oxide of lead, consists of $Pb_3 O_4$; but this is not generally considered to be a direct combination of oxygen and lead in these proportions, but a mixture of the second and third oxide just described, in the proportion of two of the protoxide to one of the peroxide, 2 Pb O + Pb O_2, which may be separated by digestion in dilute nitric acid: the acid combining with the protoxide, and liberating the peroxide which remains undissolved. Whether the view we have stated of its constitution be correct or not, is not very important, as this oxide is not much used in the dye-house. It is known in commerce as red lead or minium.

Carbonate of Lead (*White Lead*) is prepared on the large scale by exposing thin sheets of lead to the vapours of vinegar: the acid is decomposed and forms carbonic acid, which combines with the lead. This salt is sometimes used for preparing salts of lead, by dissolving it in the acid the salt of which is required.

Nitrate of Lead is prepared by dissolving litharge or metallic lead, in nitric acid, and evaporating the solution, which leaves a crystalline mass, the crystals of which are white and generally opaque, and soluble in $7\frac{1}{2}$ parts of cold water. The nitrate of lead, when prepared in this way, contains one proportion of oxide, and one of nitric acid; but by boiling the salt for some time over litharge, the acid combines with two, three, or even six proportions of lead, forming what are termed *basic* salts. This fact has been known to practical dyers for many years, and is made available for the purpose of dyeing orange colour and dark shades of yellow.

Acetate of Lead (*Sugar of Lead*) may be obtained by exposing metallic lead to the action of acetic acid, either as a

liquid or as a vapour, and to the air; a portion of the acid is decomposed, and carbonate of lead is formed, which is then easily decomposed by another portion of the acid; the latter combining with the lead, forms acetate of lead, and the carbonic acid is evolved.

Acetate of lead is prepared extensively by a variety of modes. The first is by immersing a number of sheets of lead in vinegar, so arranged that the uppermost sheets are exposed to the action of the air. When they become covered with the crust of carbonate, they are shifted to the bottom of the vat, where the acid decomposes the carbonate and forms acetate, while the succeeding sheets are being exposed to the same course of action.

Another process is to expose sheets of lead to the vapour of vinegar: the carbonate formed is collected and immersed in strong vinegar. In both these processes, when the acid appears to be saturated, or when it ceases to decompose the carbonate, the solution is drawn into proper vessels and allowed to crystallize.

Another process is to dissolve litharge in strong vinegar to saturation. This is done by gradually sprinkling the litharge in a vessel of vinegar subjected to a boiling heat; the vinegar is constantly stirred, to prevent the adhesion of the litharge to the bottom and sides of the boiler. When a sufficient quantity is dissolved, a moderate quantity of cold water is poured into the solution, reducing it a little below the boiling point, and it is allowed to settle; the clear fluid is then drawn off into a separate vessel and allowed to crystallize. If the solution be coloured, it is whitened by filtration through bone black. Common unrectified wood vinegar or pyroligneous acid, is much used for the preparation of acetate of lead for the dye-work. It is known in the dye-house by the appellation of *brown sugar*.

Basic salts, or subacetates, are made by boiling common acetate of lead with litharge. The tribasic acetate, a combination of three of lead to one of acid, is the best salt for dyeing orange, deep yellow, and amber. It is prepared in the dye-house by boiling a solution of sugar of lead with litharge, and adding to this a little lime. The proportions, however, vary in different dye-houses. Those which ought to be employed to produce the tribasic acetate, are six parts of crystallized

acetate of lead, eight of litharge, and thirty of water, boiled till the litharge is dissolved. The addition of small quantities of lime causes a loss, as the lime combines with part of the acetic acid forming acetate of lime, which, if these proportions have been used, would prevent some of the litharge from being dissolved. If the mixture be not long enough boiled, or if the proportion of litharge be too small, the addition of lime insures the conversion of the acetate of lead into the tribasic state, though it is to be observed, that this will be at the expense of a portion of the lead intended for producing the colour. We have experienced much annoyance from this source; and it is well known in the trade, that when the lead is hastily prepared for orange, it is a cause of great anxiety, and the colour obtained is frequently defective. As this is rather an important point in the economy of the dye-house, we shall explain our view of the matter. If the proportions, recommended above, be used, the following is the result: and we must bear in mind that while the oxide of lead forms the basis of the dye, the acid merely holds the lead in solution. The six pounds of acetate of lead are composed of 4 lbs. oxide of lead, and 2 lbs. acetic acid; but when the 8 lbs. of litharge are dissolved, or, as dyers say, taken up, the tribasic salt will consist of 12 lbs. of oxide of lead and 2 lbs. of acetic acid: that is, every ounce of acid holds in solution 12 ounces of oxide of lead. Now, if a little lime, as we have often remarked, be put in along with the litharge, the result will be as follows: Suppose that 50 lbs. of cotton are to be dyed orange, and that it consumed the 6 lbs. acetate of lead prepared as now stated, to give it a good colour. If $1\frac{1}{2}$ ounces of lime be mixed in, they will combine with 3 ounces of acid: in this way 36 ounces of oxide of lead are not taken up, and are therefore ineffective in the production of the colour; while at the end of the process, the dyer is surprised to find his colour poor. We may notice that lead in the basic state is not held in combination by a very great affinity, and thus a very little counteractive influence precipitates it. The presence of sulphates or carbonates in the water, which almost all water contains, precipitates the lead; hence the reason that often, when the clear acetate solution is poured into a tub of water, the contents become milk-white by the formation of an insoluble carbonate or sulphate. The lead is all lost for the time, as it is rendered insoluble and

useless as a dye. Every ounce of carbonate renders useless five ounces of lead. The softest water should be used for the lead solution, as, for example, the condensed steam from an engine. When much lime is added, it dissolves the lead, and forms a mordant quite as good, if not superior, to that described, as we will have occasion more fully to indicate when we come to treat of the processes for dyeing oranges and yellows. Alkaline salts of lead and oxide of lead dissolved in alkalis, are now becoming more generally used than the acid salts, and are superior for most purposes.

Sulphate of Lead.—Sulphuric acid, when hot and concentrated, dissolves lead; but the sulphate is precipitated by dilution. It is an insoluble white powder, easily formed by adding a solution of a soluble sulphate, as that of an alkali, to any salt of lead.

Chloride of Lead.—Lead dissolves slowly in hydrochloric acid, forming a chloride which requires 135 times its weight of cold water to dissolve it. Several sub-chlorides of lead are also capable of being formed, but they are nearly all insoluble in water.

All the soluble salts of lead are poisonous, and have a sweetish taste, except the sulphate, which is inert. Their reactions with other substances are as follows:—

Soda and potash, give.....White precipitates, soluble in excess.
Lime .....White precipitate, soluble in excess.
Ammonia .....White precipitate, insoluble in excess.
Carbonates of alkalis.....White precipitates, insoluble in excess, but soluble in caustic alkali.
Oxalic acid .....White precipitate.
Yellow prussiate of potash.White precipitate.
Red prussiate of potash...No precipitate.
Solution of galls .....White precipitate.
Chromates of potash.....Yellow precipitates.
Iodide of potassium.....Yellow precipitate.
Sulphurets of the alkalis..Black precipitates.

Testing the Value of Lead Salts.—A very simple method of testing the value of salts of lead, that is, of ascertaining the quantity of lead in a solution, is to dissolve say 10 grains of bichromate of potash (*red chrome*) in hot water, and put

the solution into a tall glass jar; then take a given weight, say 100 grains of the lead salt, whether acetate or nitrate, and dissolve in one measure (by the alkalimeter) of water; add this gradually to the chrome solution until the liquor above the precipitate becomes colourless, or until a drop of the liquor added to a drop of the lead solution on a glass plate is not turned yellow. The number of graduations taken to effect this is noted; then, as every 148·6 of bichromate of potash is equal to 379·4 acetate of lead, or 330 nitrate of lead, the quantity required by the 10 grains chrome is easily calculated—being for acetate 25·6, and for nitrate 23 grains. All the solution required above these measures will indicate impurities. The average of

Commercial nitrate requires 24· grains.
" *white sugar*, 27· "
" *brown sugar*, 28· "

The quantity of lead in a solution is tested in the same way.

Bismuth (Bi 213.)

This metal occurs in nature in the metallic state, and also in combination with other substances. When found in the metallic state, it is separated from the earths, through which it is diffused, by a melting heat—the metal sinking to the bottom of the crucible, and the earthy matters floating on the surface. It is a white metal, with a reddish hue, very crystalline in structure, volatilizes at a red heat, and burns in the air with a pale blue flame, forming oxide of bismuth. The metal does not tarnish by exposure to the air. It combines with oxygen in several proportions. The protoxide = Bi O is formed by combustion, as stated, and is of a straw-yellow colour. There is also a suboxide = $Bi_2 O$, and a peroxide = $Bi_2 O_3$, but these oxides have no corresponding salts.

Sulphate of bismuth may be prepared by dissolving the oxide in concentrated sulphuric acid. Chloride of bismuth by dissolving in hydrochloric acid; these salts are decomposed by dilution.

Nitrate of Bismuth.—Nitric acid dissolves bismuth easily,

forming the nitrate, which crystallizes in beautiful white crystals. This salt is also decomposed by water; indeed, all the neutral salts of bismuth are precipitated by adding water to their solutions, there being formed salts with the oxides.

The action of re-agents upon the solutions of bismuth is as follows:—

Potash, soda, and ammonia...White precipitates, not soluble in excess.
Carbonates of the alkalis.....White precipitates, not soluble in excess.
Yellow prussiate of potash ...White precipitate.
Red prussiate of potash .....Pale yellow precipitate.
Solution of galls.....Orange-yellow precipitate.
Iodide of potassium.....Brown precipitate.
Chromates of potash.....Yellow precipitates.
Sulphurets of the alkalis .....Black precipitates.

TIN (Sn 59.)

This metal has nearly the colour and lustre of silver; it is one of the few metals which were known to man at a very early period of his history, and was extensively used in all countries, both east and west, having any pretensions to civilization. This was probably owing to the ores of the metal being easily reduced to the metallic state, these being in general oxides; so that by merely fusing them with carbonaceous matter, such as wood or coal, which combines with the oxygen, the metal is fused, and sinks in the melted state to the bottom of the furnace.

The principal localities for obtaining tin, are Cornwall in England, Bohemia, Mexico, and the East Indies; in the former country, the metal has been wrought for many ages, and may almost be said to be the first nucleus of civilization in this country, as it formed the great mart where the civilized and commercial Phœnicians obtained the tin which was so abundantly used by them. The ore is found in Cornwall both in veins traversing the primary rocks, and in small rounded grains in the neighbourhood of these rocks, imbedded in what geologists term the *alluvial deposit*, signifying the deposit formed by the washing

away of the fragments of the primary rocks with water. This gives the purest tin, and is distinguished by the name of *stream* tin. The ore obtained from the veins is generally contaminated with other metals, such as iron, copper, arsenic, and the like, but is partially purified by liquation, that is, by heating the mass to the melting point of tin, which melts out and leaves the others. Several other operations of refining follow this, which need not be detailed; but there are always some few of the impurities remaining in a portion of the tin. That portion which contains these impurities, is termed *block* tin. The pure *grain* tin is heated till it becomes brittle, and is then let fall from a height, which splits it into small bars or prisms, and in this state it is found in commerce. These bars in bending, make a peculiar crackling noise, and become heated; phenomena probably owing to the separating of their parts, and the sudden fracture caused by bending.

Tin is very extensively used in dyeing and printing both cotton and woollen. Its introduction as a mordant may be considered as forming an era in the art of dyeing, and like many other important improvements in this art, was the result of accident, an account of which is given by Berthollet as follows:—"A little while after the cochineal became known in Europe, the scarlet process by means of the solution of tin was discovered. It is stated that about the year 1630, Cornelius Drebbel observed by an accidental mixture, the brilliancy which the solution of tin gave to the infusion of cochineal. He communicated his observation to his son-in-law, Kuffelar, who was a dyer at Leyden. He soon improved the process, kept it a secret in his workshop, and brought into vogue the colour which bore his name."

Soon afterwards, a German chemist found out the process of dyeing scarlet by means of the solution of tin. He brought his secret to London in 1643; it became known to others, was soon afterwards diffused over Europe, and its applications became more extended, as whenever a new dye drug was introduced into the art, the solution of tin was universally applied, by which means it became a standard mordant for the various dyewoods, such as logwood, Brazil wood, and the like.

Copper boilers used for dyeing woollen and silks, have generally a part covered with or made of tin, which is in-

tended to prevent the acid mordant from acting upon the copper, and this it does, by a galvanic action, the tin being slowly acted upon, while the copper is protected.

Tin combines with oxygen in three different proportions—

Protoxide..... Sn O.
Sesquioxide..... $Sn_2 O_3$.
Peroxide..... $Sn O_2$.

There are salts of tin corresponding to these oxides, all more or less useful in dyeing.

Protoxide of Tin is formed by precipitation from a solution of the protochloride of tin by carbonate of potash or soda. It is obtained as a white powder, which is a hydrate of the oxide, and which, if heated to 176°, loses its water of combination and becomes black, and may be kept in this state; but if brought to a red heat, or into contact with a red hot body, it takes fire, and in burning passes into the state of peroxide. The white hydrated oxide is easily dissolved in acids, and also in solutions of the alkalis, but these alkaline solutions are not permanent: for if diluted with water, a portion of the tin is precipitated, and another portion passes into the state of peroxide. Also, when brought into contact with other oxides which yield their oxygen freely, such as peroxide of iron, a reaction takes place: the iron is reduced to a lower state of oxidation, and the tin is raised to a higher. These reactions and properties are taken advantage of in many of the operations in dyeing.

The protoxide of tin and its protosalts all come under the denomination of *stanous salts:* and it may be remarked of them, as a general characteristic, that they all absorb oxygen from the air by exposure.

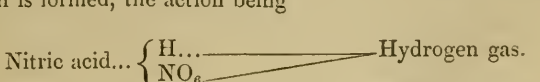
Protochloride of Tin, (*Salts of Tin.*)—This salt is prepared by dissolving tin in strong hydrochloric acid, with the assistance of heat, the solution evaporating and crystallizing in the ordinary way. The crystals were formerly said to contain three proportions of water, about 22 per cent.; but according to a recent investigation by Dr. Penney, they contain only two proportions. The crystals dissolve in a small portion of water; but if put into a large quantity, the whole becomes milky, and a white powder separates, which is an oxychloride of tin. A complete and clear

solution of salts of tin in water cannot be retained for any length of time on account of the great attraction which this salt has for oxygen. A little hydrochloric acid put into the water, however, has the effect of greatly retarding, and, indeed, of almost wholly preventing this decomposition. In establishments where the dyers prepare their own *salts of tin*, they do not crystallize it, and as there is nearly always an excess of acid, some of the phenomena mentioned may not have been observed.

On adding potash to salts of protochloride of tin, a double salt is formed of chloride of tin and chloride of potassium, which may be crystallized.

Protosulphate of Tin.—Sulphuric acid dissolves tin slowly, and forms a thin pasty-looking mass, which, by evaporation, yields crystals. This salt is not used in the dye-house; it is, indeed, immediately decomposed by aqueous dilution.

Protonitrate of Tin.—Protoxide of tin dissolves easily in dilute nitric acid, but it cannot be concentrated, from its liability to pass into the state of peroxide. When nitric acid of specific gravity 1·114 = 23 of Twaddell, is poured upon the metal, it dissolves it rapidly, and much heat is evolved, which ought to be kept down by placing the vessel containing the acid in cold water. If this be properly done, a protonitrate of tin is formed, the action being



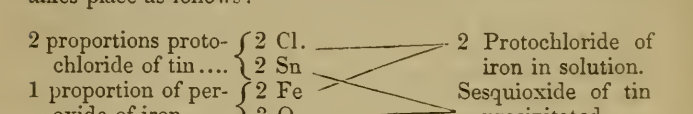
But should the heat be allowed to rise too high, the nitric acid is also decomposed, and the tin passes into a higher state of oxidation. Also, if the action is very rapid, ammonia is formed between the hydrogen and nitrogen, and consequently a double salt of tin and ammonia; but the greater proportion of the tin is precipitated as a white pasty mass of peroxide.

Tartrate of Potash and Tin is prepared by dissolving protoxide of tin in bitartrate of potash, (*tartar*, or *cream of tartar.*) This forms a very soluble salt, occasionally used in dyeing woollens; but in this case the *tartar* is added to the salts of tin.

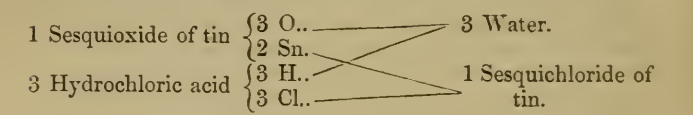
A combination of the protoxide of tin, arsenic, and soda

has recently been patented as a salt in calico-printing, under the name of STANO-ARSENITE OF SODA.

Deutoxide, or Sesquioxide of Tin = $Sn_2 O_3$, can be prepared by adding to a saturated solution of protochloride of tin some newly-precipitated peroxide of iron: a double decomposition takes place as follows:—



Strong hydrochloric acid dissolves this oxide, and forms with it a sesquichloride, thus:—



The other salts corresponding to this oxide have not been examined; but the distinctive character of the oxide itself may be made evident by the two following reactions:—Ammonia dissolves this oxide, but does not dissolve the protoxide; and hydrochloric acid dissolves this oxide, but does not dissolve the peroxide. There can be little doubt but that an investigation into the sesquioxide and its salts would explain many of the hitherto unexplained phenomena of dyeing; and that it is highly probable the formation of salts of this class play a considerable part in many dyeing operations; such as those processes in which chloride of tin is mixed with pernitrate of iron, as for royal blues, &c.

Peroxide of Tin.—The ores of tin, termed *tinstone*, are mostly peroxide. They are black, shading to brown: in this state the oxide is not soluble in acids, but becomes so by previous ignition with an alkali.

When metallic tin is put into dilute nitric acid, and the action allowed to proceed rapidly, or when heat is applied, there is formed a hydrated peroxide, as a white mass, which contains 11 proportions of water. Dilute hydrochloric acid dissolves this oxide slightly, but it is not soluble in nitric or sulphuric acids. If acted upon by hydrochloric acid, and allowed

to stand for some time, and the supernatent liquor then poured off, the remaining insoluble oxide is soluble in water. If this hydrated peroxide be dried with heat, it loses its water, and passes into the same state as the ore. Boiling water, poured upon it, will effect similar changes.

The peroxide of tin is obtained easily by precipitation from a solution of bichloride, by adding an alkaline carbonate. Thus prepared, and in this condition, the peroxide is easily dissolved in hydrochloric acid, either strong or dilute; but if this oxide be heated in any way, as by pouring boiling water upon it, strong hydrochloric acid will not dissolve it, and dilute acid only partially. The oxide has now indeed every property that it has when formed by the nitric acid process. It is also soluble in pure water, after being made into a paste with strong hydrochloric acid, but the addition of a little of this acid to the watery solution will precipitate it.

The changes effected upon this oxide by heat or applying boiling water, are supposed to be owing to its state of hydration; but be that as it may, these peculiarities ought to attract the attention of the practical dyer; as the annoyances to which they give rise are very considerable, and only require the exercise of a little care to be avoided. The hydrated peroxide of tin is very soluble in caustic alkalis.

The peroxide of tin has been termed *stanic oxide* and *stanic acid*, as it has certain acid properties. It combines with alkalis, and forms salts.

Perchloride of Tin, (*Permuriate of Tin.*) — When tin is dissolved in a mixture of hydrochloric and nitric acids, the salt formed is generally the perchloride = $Sn\,Cl_2$, and is consequently that most generally used in the dye-house, where almost all salts are prepared by a mixture of the acids. But from what has been stated in reference to the separate oxides and salts, it will be evident that this subject stands in need of further investigation; the modes of preparation are so varied in the proportions of each acid, in the qualities of tin used, and in the manner of adding the tin; all and each of these circumstances, it will be observed, make a difference. If tin is added too rapidly, the action and heat may be so violent as to precipitate some of the oxide in an insoluble state; if added too slowly, and at a temperature too low, there may be protochlorides formed, or mixtures of the differ-

ent salts, in very varied proportions; and hence the cause of the irregularity both in quality and kind of colour produced by tin mordants. Perchloride of tin is generally formed by dissolving crystals of the protochloride in a small portion of water, adding nitric acid, and applying heat, or by passing a stream of chlorine gas through a solution of salts of tin. These are termed in the dye-house oxychlorides of tin.

Dr. Penney, in a recent communication to the Chemical Society, has recommended a simple means of testing the quantity of tin present in a solution of salt in the proto-state, founded upon the reduction of chromic acid to oxide of chromium, by protoxide of tin. The method recommended for *salts of tin* is the following:—100 grains of the crystals are put into a vessel with 20 oz. of water, and half an ounce of hydrochloric acid; 83½ grains bichromate of potash are dissolved in warm water, and placed in an alkalimeter, the whole measuring 100 graduations; this solution is added by degrees to the solution of tin, which takes a rich green colour. The solution of chrome is added, until a drop taken out and put upon a drop of acetate of lead, on a glass or paper surface, gives yellow. If the tin solution is more dilute, and put into a large glass jar, the green tint, whenever the chrome is in excess, is perceptibly yellow. A little experience renders the operation simple. The quantity of bichromate (83½ grains) is equal to 100 grains of pure metallic tin; hence every graduation of the chrome solution taken to effect the change described, is equal to one grain of tin. As 83½ grains of bichromate of potash may not be soluble in one measure of the commonalk alimeter, two measures may be taken; in that case, two graduations will indicate one grain of tin in the salt tested.

Solutions of tin, such as are sold to calico-printers, under the term *single* and *double muriates* may be tested by taking a measured quantity of the solution and treating it in the same manner Or, as recommended by Dr. Penney, by taking a weighed quantity of the solution of tin, say 500 grains, and making up with water to fill the alkalimeter; then dissolve 41·6 grains of bichromate of potash in warm water, and add the solution of tin to this very cautiously, as long as the tint remains of an olive-green colour, or until a drop taken out and added to a drop of lead

in solution gives a yellow colour. Whenever the yellow ceases to be obtained, the operation is complete. Finally, by dividing 1000 by the number of graduations taken of the tin solution, the per centage of the tin is ascertained. Thus, say that 41·6 of bichromate of potash required 38 graduations of the tin solution to reduce the chromic acid, then

$$38)1000(26{\cdot}3 = \text{per centage of tin in solution.}^*$$

This test only applies to tin in solution in the proto-state, but gives no change in the persalts of tin, and is therefore not applicable to many of the *spirits* used in the dye-house.

Spirits.—The solutions of tin, in the technical language of the dye-house, are termed *spirits*, with an affix to each mode of preparation, to denote their special application, such as red spirits, yellow spirits, plumb spirits, &c. The preparation of these spirits is a matter of much pride amongst dyers, and each has some little peculiarity which he keeps to himself, and on the virtue of which he supposes all his success depends. These peculiarities are generally in the proportion of the acids and the tin, and the manner of mixing them. However, as may be supposed, they are not equally answerable for all the purposes to which they are applied; hence the reason that we find one dyer best at reds, another at purples, another at blacks, and another at browns.

We will here give a few practical methods of preparing these several spirits, reserving our remarks upon their varieties and effects, to our general observations on mordants, to which we will devote a separate chapter, in order that we may be able to go fully into the subject.

The first process in preparing spirits, is to *feather* the tin. This is done by melting it in an iron ladle, and pouring it, when in a melted state, into a vessel filled with cold water, the hand to be held as high as possible, so that it may pour more in drops. The appearance of the tin in this state is beyond description beautiful. By this process of feathering, a very extended surface of metal is exposed to the acid, which facilitates its solution very much.

Red Spirits.—If red spirits be wanted, that is, a mordant for dyeing red upon cotton by Brazil-wood, the general

* Journal of Chemical Society, for 1851.

method is to take three measures of muriatic acid, and one of nitric acid, then add the tin by degrees to this mixture so long as the acids continue to dissolve the metal; care ought to be taken not to add it too rapidly, but bit by bit, adding one piece just as the other is dissolved. We know that this is not generally attended to, as one handful of the metal is put in after another, at certain and too often irregular intervals of time, giving very annoying results. When the metal is put in too rapidly, or too much at once, the action becomes violent, the solution gets heated, the nitric acid is decomposed, ammonia is formed in the solution, and when the solution cools, a quantity of peroxidized tin falls to the bottom, as a gelatinous precipitate, creating much loss. When spirits thus prepared are used for a brilliant red upon cotton by Brazil-wood, the proper hue is never obtained, the colour being always more or less brownish. The proportions of the acids for preparing the red spirits, are not invariably three to one, the mixture varies from half-and-half to five to one, depending upon the taste and experience of the dyer. Some dyers only dissolve a given quantity of the metal to the pound weight of the mixed acids, varying from one-and-a-half to three ounces to the pound; but according to our experience, the acids, in whatever proportions they are mixed, ought to be saturated, at least so far as they will become saturated, observing the precautions described above. We have also found that when much nitric acid is used, the reds are generally deeper in colour, and have a very great tendency to turn brown, especially if the goods be dried by heat; but when the muriatic acid prevails, the colour obtained has more of the crimson or rose tint, and is not so liable to become brown in drying.

Plumb Spirits.—This solution is prepared by dissolving tin in hydrochloric acid diluted with about a seventh of water, adding two ounces of tin to every pound weight of acid. The tin, as in other cases, ought to be added gradually. Some, however, add nitric acid, and prefer it thus mixed, and others add as much tin as the acid will dissolve cold.

Barwood Spirits.—The method given for the preparation of this solution is six measures muriatic and one of nitric acid, adding tin gradually until white bubbles begin to rise to the surface, allowing the solution to stand for twelve hours before

using it, a rather uncertain test of quantity of tin, and of the quality of the spirits.

Yellow Spirits.—This solution is now seldom used; it was applied as a mordant for the dyeing of yellow by quercitron bark, and was merely the substitution of sulphuric acid for the nitric acid of the common red spirits. It was proposed by Dr. Bancroft as a question of cheapness in the preparation of scarlet spirits, and was afterwards much used, as stated, for dying yellows, as its name implies. By this method of preparation, the tin was generally in the proto-state, which gave it a peculiarity in relation to the common red spirits, as it afforded bluer tints with red woods when used as a *raising* or *alterant*. The tin spirits, as double and single muriates, the salts of tin dissolved in water and muriatic acid, and the metallic tin dissolved in hydrochloric acid, (*plumb spirits*,) all have the same effect. Some dyers, however, use the red spirits for alterants and dyeing yellows.

Instead of using hydrochloric acid for preparing spirits, many woollen dyers use sal-ammoniac or common salt, adding it to nitric acid in the proportion of 6 lbs. nitric acid to 1 of water in which 1 lb. sal-ammoniac is dissolved, and then adding 10 oz. of tin.

Acetate of Tin is prepared by adding a solution of acetate of soda to protochloride of tin; common salt is formed and acetate of tin; the former is not hurtful to the dyer.

Oxalate of Tin may be formed in the same way, by using oxalate of soda, or by dissolving precipitated protoxide of tin in oxalic acid.

In dissolving tin in hydrochloric acid, it is often observed that towards the end of the process, when the tin is in the solution, parts of the metal seem to dissolve, while other parts become coated with a crystalline substance, soluble only with much difficulty, and occasioning both annoyance and loss. This is caused by one portion of the solution becoming denser than other portions, a galvanic action being induced between those parts of the tin in the weaker portion of the solution, and the parts in the stronger, consequently depositing the tin upon the metal in the strongest parts of the solution. This evil can be prevented by occasionally stirring the solution.

The following is the reaction of solutions of other substances on the protosalts of tin:—

Potash and soda .....White precipitates, soluble in excess.
Ammonia ..... ditto, insoluble in excess.
Carbonates of the alkalis... ditto, soluble in caustic alkali.
Yellow prussiate of potash, White precipitate.
Red prussiate of potash ... ditto.
Galls in solution.....Slight yellow precipitate.
Chloride of gold.....Deep purple precipitate (purple of cassius.)
Sulphurets of alkalis .....Brown precipitates.

With the persalts of tin—

Potash and soda .....White precipitates, soluble in excess.
Ammonia ..... ditto, ditto.
Carbonates of the alkalis... ditto, soluble in caustic alkali.
Yellow prussiate of potash..No precipitate.
Red prussiate of potash ... ditto.
Solution of galls..... ditto.
Sulphurets of the alkalis...Yellow precipitates, soluble in caustic potash.

TITANIUM (Ti 25.)

This metal was discovered in 1791. It is generally found in nature in combination with iron; a great number, indeed, of the iron ores of this country seem to contain traces of this metal. It regularly makes its appearance in the blast furnace; but its proportion in the foregoing ores is so minute, that no chemist has yet detected it in analyzing them; and it has not been found in any great quantity. It is not dissolved in any acid except *aqua regia*, a mixture of nitric and hydrochloric acids. It combines in two proportions with oxygen, forming

Protoxide..... = Ti O.
Peroxide..... = Ti O_2.

The latter oxide, on account of its combining with the alkalis and forming soluble salts with them, has been termed titanic acid.

The salts formed by the action of acids upon this metal have not been much studied; those which have been investigated

most carefully are the salts formed by the peroxide or titanic acid. Solutions of these salts give a brown precipitate with galls; but all the compounds of this metal are very untractable, and being besides very scarce, they are of little use in the arts.

Chromium (Cr 26·7.)

This metal is found in considerable quantities in nature, combined with lead and iron. The latter (chrome iron) is its principal ore. It is found in America and in different parts of the Continent of Europe; also in Shetland, and in Fifeshire in Scotland. The composition of the ore is $FeO + Cr_2O_3$.

The metal was discovered in 1797 by Vauquelin. It approaches to cast iron in appearance, but has only been obtained in the state of powder. It is very difficult to fuse, and does not undergo oxidation by exposure to the air. The metal is not acted upon directly by the common acids; but may be obtained in combination with acids, by decomposing some of its salts or oxides, of which there are two, namely—

Peroxide.....Cr_2O_3.
Chromic acid.....CrO_3.

The last (chromic acid) forms the acid of the salts named chromates. The oxide of chromium exists combined with iron in the ore, as stated above; it is not, however, obtained from the ore, but by acting upon some of the salts of chromic acid. It is of a beautiful green colour, and may be prepared by various methods; *e.g.* take

1 part bichromate of potash,
$1\frac{1}{2}$ parts sal-ammoniac,
1 part carbonate of potash,

and ignite this mixture in a crucible: the chromic acid is decomposed, and the oxide formed. By digesting what remains in water, the oxide is obtained as an insoluble powder. Another and more easily-practised method for the dye-house, is that adopted on the Continent, and is as follows: Take 9 lbs. of bichromate of potash, and dissolve in 5 gallons of boiling water; then, into a boiler containing 23 gallons of boiling

water, put 10 lbs. of the white oxide of arsenic; boil for ten minutes, and allow the liquor to settle. The *clear* is then mixed with the solution of bichromate of potash, stirring all the time, when very soon the hydrated oxide of chrome is formed, and precipitated. After the whole is cool, it is put upon a filter, and the oxide which remains upon the filter is washed with boiling water. If a little hydrochloric acid be added, the chrome oxide is obtained as a green solution. This oxide has long been used to give a green colour to glass and porcelain, and has lately been introduced and is now extensively used in calico printing. It is also partially used in the dye-house for dyeing colours of various tints, all of which have the valuable property of permanency.

Chloride of Chromium.—The oxide of chromium dissolves readily in hydrochloric acid, and forms a chloride, which has a deep green colour and a strong acid reaction. Evaporated nearly to dryness, there are produced red coloured scales, which give a green solution with water. The following method for the preparation of the chloride has been recommended: Hydrochloric acid is diluted with water until the acid no longer gives off fumes; it is then heated, and when hot, as much of the oxide of chromium, prepared by the arsenic solution, is added, as the acid will dissolve; the whole is then left to settle, and the *clear* is taken off. This contains some free acid, which would act upon the cotton fibre; to remove it, and obtain the salt in a neutral state, potash ley is poured in gradually, until the oxide of chromium begins to be precipitated. The solution thus prepared has a dark green colour, and is used for several operations in dyeing. Preparations of this salt or rather mixture of salts, have been long used in calico printing. These are made by mixing together chromate of potash, hydrochloric acid, and tartaric acid, in a great variety of proportions, giving green tints of various depths according to the mixture used.

Sulphate of Chromium.—Sulphuric acid added to oxide of chromium dissolves it, and forms a green coloured solution, which does not crystallize. If evaporated to dryness, it loses its solubility in water; but by adding sulphate of potash or a solution of potash, taking care not to precipitate any of the oxide, there is formed a double salt, termed *chrome alum*. The solution of this double salt is a blueish purple; it

crystallizes easily, giving dark purple coloured crystals; but care must be taken that the solution is not heated to the boiling point, as it is thereby turned green, and yields no crystals.

Oxalate, acetate, tartarate &c., of chromium, may be obtained by dissolving the oxide in any of these acids; they all give green coloured solutions. If we mix together one part of bichromate of potash, two of crystallized oxalic acid, and two of binoxalate of potash, and dissolve the mixture in boiling water, a salt is formed, which crystallizes in nearly black coloured crystals. It is a double oxalate of chromium and potash.

Chromic Acid.—Salts of this acid are prepared directly from the chrome iron ore; and the acid is obtained by decomposing these salts. Chromic acid is of a beautiful deep orange colour, approaching to scarlet, and may be obtained in a crystalline form. Various methods have been proposed for preparing it; the following, by Mr. Robert Warrington, is probably the most simple:—"Take 100 measures of a cold saturated solution of bichromate of potash (prepared by boiling, and then allowing the solution to cool and deposit the excess of the salt), and add to this from 120 to 150 measures of concentrated sulphuric acid; the latter should be free from sulphate of lead, as otherwise it would fall as chromate and sulphate of lead with the chromic acid on dilution with the bichromate. The mixture is then allowed to cool, and the chromic acid gradually crystallizes in beautiful dark crimson needles. Decant the fluid part, and place the crystals with the adhering sulphuric acid on a thick flat tile of biscuit porcelain: another tile is then to be placed upon the crystals, and the whole submitted to a pressure for a considerable time. On removing the chromic acid, it will be found in a perfectly dry state, and yielding a mere trace of sulphuric acid on examination." *

Chromic acid may also be prepared from the chromate of lead, which results from the mixture of a salt of lead and bichromate of potash at the bottom of the *chrome tubs* used in dyeing yellows. Two parts of strong sulphuric acid being added to one part of dry chromate of lead slightly heated, and allowed to stand for about twelve hours; water is then

* Proceedings of the Chemical Society, vol. i.

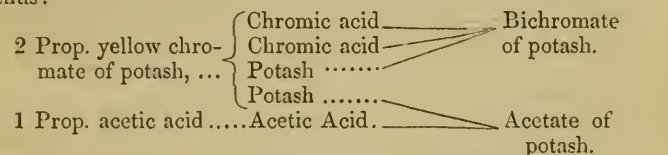
added, when the lead is precipitated as a sulphate, and the chromic acid, mixed with a little sulphuric acid, remains in solution. The liquid is decanted and evaporated at a boiling heat; on cooling, the greater portion of the chromic acid separates in beautiful carmine-red crystals. If the process be carefully conducted, a great portion of what is now little better than thrown away, might be made useful by a trifling addition of expense. Another method of preventing waste is to add potash to the solution, so as to form chromate and sulphate of potash, which may afterwards be separated by crystallization.

Chromic acid combines with the different bases, and forms a series of important salts. With potash it combines in two proportions, forming what is termed the yellow and the red chromate of potash. The yellow chromate of potash may be prepared by adding to two pounds of red chromate one pound of caustic potash; it crystallizes in small crystals of a rich deep lemon colour, composed of one proportion of acid and one of potash. This salt is not much used in the arts.

Bichromate (Red Chromate) of Potash.—This salt may be prepared from the yellow chromate by adding a little sulphuric acid, which combines with a portion of the potash, leaving two proportions of chromic acid in union with one proportion of potash, which crystallizes in large square tubular crystals of a rich orange-red colour. This is the salt used in the arts, not only for dyeing, but for the preparation of other chrome compounds, and is prepared on the large scale in the following manner. Chrome iron ore, after being finely ground and sifted, is mixed with a quantity of dried nitrate and carbonate of potash. This mixture is thrown into a reverberating furnace, and subjected to a powerful heat, being occasionally stirred. When perfectly calcined, the mass is raked out and dissolved in water. It is then boiled for several hours, after which the insoluble portion is allowed to settle, and the solution decanted; this is evaporated, and leaves the yellow chromate of potash crystallized. The chemical changes which take place in the furnace are these: first, the decomposition of the nitre, giving off oxygen, which combines with the oxide of chromium, and forms chromic acid; this unites with the potash of the nitrate and of the carbonate, and forms the yellow salt which is soluble in water, and afterwards separated as de-

scribed. It contains also soluble impurities, such as caustic potash, silicate and aluminate of potash, which are separated by the succeeding operations of boiling and crystallization.

The bichromate, which is the salt used in dyeing, is prepared from the yellow salt obtained as above. Into a concentrated solution is poured acetic, or sulphuric acid. The latter acid, though often used, is not well adapted for the purpose, as the sulphate of potash formed is very difficult to separate from the chromate, and constitutes a serious adulteration. Acetic acid is preferable, and is now generally employed. The quantity of the acid is so regulated, that it combines with the one-half of the potash in the yellow salt, leaving two proportions of chromic acid in union with the other half; this process may be expressed thus:—



The solution of yellow chromate being concentrated before the addition of the acetic acid, the bichromate formed has not so much water as will hold it in solution, and is therefore thrown down as an orange-coloured powder; this is carefully collected, dissolved in water, and crystallized by slow evaporation.

When the bichromate of potash has been prepared by sulphuric acid, as we stated above, it is very liable to contain sulphate of potash, and that often to a great extent. This salt may be detected by dissolving a small quantity of the chromate in distilled water, adding to it a little pure nitric acid, and then nitrate of barytes, which will give a white precipitate if a sulphate be present. The solution used in testing should be much diluted. If any chloride of potassium be present, it may be detected by adding a little nitrate of silver to a solution of the chromate, similarly prepared by having a little nitric acid added to it; in this case a white precipitate results.

Soda has been tried in the preparation of this salt to form a bichromate of soda, which might be equally useful to the dyer, but this base is not used for the reasons already assigned at page 127.

Chromate of Lead.—The chromates of other bases or metals are obtained by adding solutions of their salts to solutions of either the yellow or red chromate of potash. For example, when a salt of lead, *e. g.* the acetate or nitrate, is added to a solution of bichromate of potash, the chromate of lead is formed and precipitates as a yellow powder, constituting the *chrome yellow dye.* If this yellow precipitate is digested in hot caustic ley, a basic salt of lead and chromium is formed, having two proportions of lead and one of chromic acid: it is therefore a subchromate of lead. This is a deep orange precipitate, approaching to a scarlet, and constitutes the *orange dye.* If a little chromate of lead (the grounds of the chrome tub) be dried, and added to some fused nitre in a crucible as long as effervescence and red fumes are observed, and the melted mass is then poured out, there will be at the bottom some subchromate of lead, which may be washed out by water; it is of a rich vermillion red, far superior to anything we have ever seen as a dye. We would recommend it for trial.

Chrome Yellow.—The chromate of lead has almost completely superseded the use of vegetable dyestuffs in dyeing yellow, orange, and green, upon cotton fabrics. To dye a yellow, the goods are immersed or wrought through a solution of either acetate or nitrate of lead, from which, after being tightly wrung or pressed, they are passed through a solution of bichromate of potash, by which the chromate of lead is formed upon and within the fibre. The goods are put several times through this operation when deep shades are required; or, what is now more generally practised, the lead is added to lime as long as the precipitate formed is re-dissolved, and the goods are wrought through this solution, and then passed through the bichromate solution; or the lead may be dissolved in potash or soda. Other qualities of yellow are also obtained by adding hydrochloric acid to the solution of bichromate of potash, distinguished as *acid yellow.* When dyeing yellows with the acid salt of lead, and passing into the chrome solution, there is a great quantity of chromate of lead formed which is not in the fibre: this precipitates to the bottom, and causes considerable loss. We have already shown that this chromate of lead may be used for making chromic acid; it is very soluble in alkalis, and may be made useful in that way also in the dye-house. When this method of dyeing is practised, there is a liabi-

lity to inequality of tint. The chromate solution is not renewed each time, only a little addition of the chrome salt made for each parcel of goods passing through the dye, and therefore there follows an accumulation of free acid in the solution which re-acts upon the colour, varying the tint of different lots. So well are these circumstances known in practice, that if yellow of a red tint is required, or what is termed *amber*, nitrate of lead is used in preference to the acetate in proportion to the depth of redness. This gives free nitric acid in the dye, which acts more than the acetic acid upon the bichromate solution. The same effects are produced by adding a little nitric acid to the chrome solution. The action of the nitrate of lead added to bichromate of potash may be thus stated. Suppose that 100 lbs. of cotton goods are to be dyed yellow, and that they get 165 ounces nitrate of lead, which is all taken up by the cotton: this will require 74 ounces of bichromate of potash. For, taking their equivalents,

165 Nitrate of lead one equivalent....	1	103 Pb...	Chromate of lead.
	$\frac{1}{2}$	NO_6 31...	Nitric acid free.
	$\frac{1}{2}$	NO_6 31...	
74 or one-half equivalent of bichromate of potash	$\frac{1}{2}$	$50\frac{1}{2}$ Cr O_3	
	$\frac{1}{2}$	$50\frac{1}{2}$ Cr O_3	
	$\frac{1}{2}$	$23\frac{1}{2}$ KO...	Nitrate of potash.

All the lead used is not imbibed by the cotton, therefore much less bichromate is required than that given here, but the action is not altered in relation to the lead really fixed upon the goods. The same reaction takes place when acetate of lead is used, but the free acetic acid does not act so powerfully upon the chromate of lead forming the dye. When subsalts of lead are used, the action is more regular, as no acid is liberated—hence the decided preference now given to these salts in dyeing. The action is represented thus—

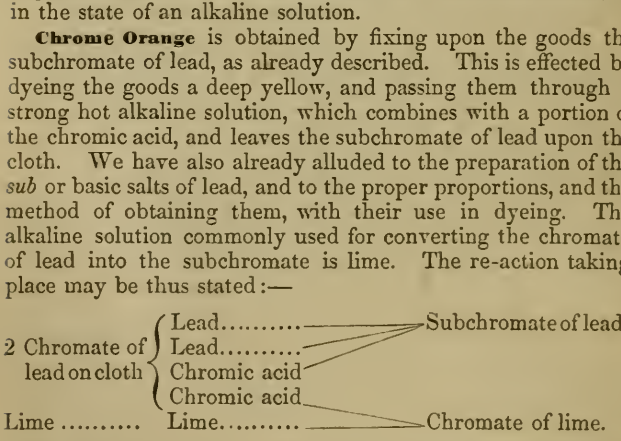
Subacetate of lead	Acetic acid...	Acetate potash.
	Lead, ...	
	Lead,.....	
Bichromate of potash.....	Potash, ...	
	Chromic acid,	Chromate lead.
	Chromic acid,	Chromate lead.

Were we dyeing 100 lbs. of cotton in different parcels, one

after the other, without changing the liquor, the last parcel would have the same chance as the first of being uniform in the colour, but not so, when each parcel is accumulating free acid, which reddens the colour. These formulæ also enable us to appreciate the use of alkaline solutions of lead—a practice now often adopted.

Chrome Greens are dyed in the same manner as the yellow, the goods being previously dyed blue by means of the blue vat. For dyeing green, nitrate of lead is never used, the free nitric acid would destroy the indigo, besides anything that tends to redden the hue is carefully avoided, so that the goods are not allowed to stand for any time out of the solution of the bichromate; yet with the greatest amount of care, there is much difficulty in avoiding brown blotches and light parts when acid salts of lead are used; but there are fewer of these difficulties experienced when the lead is either in a subacetate state, or in the state of an alkaline solution.

Chrome Orange is obtained by fixing upon the goods the subchromate of lead, as already described. This is effected by dyeing the goods a deep yellow, and passing them through a strong hot alkaline solution, which combines with a portion of the chromic acid, and leaves the subchromate of lead upon the cloth. We have also already alluded to the preparation of the *sub* or basic salts of lead, and to the proper proportions, and the method of obtaining them, with their use in dyeing. The alkaline solution commonly used for converting the chromate of lead into the subchromate is lime. The re-action taking place may be thus stated:—



The following receipt will produce a good orange upon a hundred pounds weight of cotton:—

Thirty lbs. of brown sugar of lead, and seventeen lbs. of litharge, are put into a boiler with about 12 gallons of water, and boiled together for an hour or so, until the litharge is dissolved; then a quantity of lime, from one to two pounds, is added, any sediment formed is allowed to settle, and the clear

fluid drawn off and put into a tub; 12 lbs. bichromate of potash are dissolved in another tub. Two other tubs, capable of allowing 10 lbs. of yarn to be wrought in them with freedom, are filled, one with water, to which a little of the lead solution is added, and the other with lime-water; 10 lbs. of the yarn (a bundle) is now wrought for some time through the tub containing the lead, wrung out, and put through the lime-water; a little more lead is added, another bundle is passed through the same tub, renewing the lime-water each time. The whole are passed two or three times through this operation, according to the depth of orange wanted. The bundles are next wrought through a tub of water, to which is added some of the solution of the bichromate of potash, then passed through the lead solution, and again through the chrome. A saturated solution of newly slaked lime is brought to the boiling point; in this the yarn is wrought, either by drawing some off in tubs, or by the most convenient method that circumstances will allow, until the colour is changed to a deep orange or scarlet. It is then taken out, passed through another tub filled with boiling water, to which is added a small quantity of solution of soap, soda, and oil; afterwards it is wrung out and dried at a high temperature. The *raising* of the orange, as the hot limeing is termed, is the most trying operation. If the lead has not been properly prepared, or if there be any mismanagement in the operation of fixing it upon the fibre, the hot lime will take all the colour off, leaving but a red salmon shade. Or if the goods are unequally dyed, the colour will come off in parts; and, what is still more frequently the case, the chromate of lead being entirely soluble in lime-water at a temperature a little under boiling, if the lime solution is allowed to become too cold, the colour will be discharged. The lime-water ought to be at the *spring of the boil*, and as we have seen, (page 134) the higher the temperature, the less lime is held in solution, consequently less risk of failure. Great care is necessary, for an orange being once wrong, it is very difficult to recover.

Bichromate of potash has been very extensively used of late as a mordant for a variety of colours upon woollen, and is entirely superseding several of the old processes for dyeing many of the ordinary shades, which were very tedious in manipulation. It is also extensively used for dyeing catechu browns

upon cotton. We may mention that working much with solutions of chrome and lead is very injurious to the hands, especially if there be any part of the skin broken, producing often very severe sores; a solution of *gutta percha* applied over the sore, forming an artificial skin, has the effect of preventing this annoyance.

Tests for Bichromate of Potash.—Tests for the strength and quality of bichromate of potash may easily be formed, thus:—Take pure nitrate of lead, say 165 grains, and dissolve in 200 measures of water; this ought to precipitate 74 grains of bichromate; so that it is merely required to dissolve 74 grains of bichromate of potash, and adding the nitrate of lead solution as long as any precipitate takes place; if all the lead is requisite, the chrome is good, but every three graduations of the lead solution left, after precipitating all the chrome, will represent about one per cent. impurity of the bichromate; or the same method may be taken as described for lead, (page 177.) These operations are easy, and may be performed by any practical dyer, although little acquainted with chemical manipulations.

The following is the reaction of salts of oxide of chromium with other substances in solution:—

Potash and soda	Greenish precipitates, soluble in excess.
Ammonia	Blue precipitate.
Carbonates of the alkalis	Light-green precipitates.
Yellow and red prussiates of potash	No precipitates.
Solution of galls	Greenish precipitate.

The reaction of bichromate upon re-agents is as follows:—

Solutions of lead	Yellow precipitates, soluble in potash.
Silver salts	Red brown.
Zinc	Forms with these salts a double salt, which is brown, and crystallizes.

VANADIUM. (V 68·6.)

This metal was discovered in 1830. It is found in nature combined with lead and iron, but is exceedingly rare. Small

samples of its oxide, termed Vanadic Acid, are sold at 1s. 6d. a grain. It has a strong resemblance to chromium in many of its chemical characters, and combines with oxygen in three proportions :—

Protoxide = V O.
Peroxide = V O_2.
Vanadic acid = V O_3.

There is no combination of vanadium with an acid corresponding to the protoxide, but there are salts corresponding with the peroxide; these, in solution, produce with

Ammonia.....Brown precipitate.
Yellow prussiate of potash.....Yellow precipitate.
Red prussiate of potash.....Green precipitate.
Galls.....Blue-black precipitate.
Sulphurets of the alkalis .....Brown-black precipitate.

Vanadic acid combines with the alkalis, and forms a variety of coloured salts, nearly all soluble in water. All the reactions of the compounds of this metal give strong hopes that, were it found plentifully, it would become a useful substance in the hand of the dyer; although in the meantime, from its price, it is of no importance to him.

Tungstenum or Wolfram. (W 95.)

This metal has the appearance of iron, and exists in nature chiefly in combination with lime. It is the dearest metal next to gold and platinum. It combines with oxygen in two proportions :—

Binoxide of Tungsten = W O_2
Tungstic acid..... = W O_3.

Binoxide of tungsten is a brown-red powder, which does not dissolve in acids, and there are, therefore, no salts of tungstenum corresponding to this oxide. The oxide passes readily into the state of tungstic acid by combining with more oxygen; and it is in this state that it is found in nature forming a tungstate of lime. By dissolving this mineral in hydrochloric acid, the lime is dissolved, and the tungstic acid remains as a yellowish powder, which combines with alkalis,

and forms soluble salts. Acids added to these salts give yellow precipitates, whereas salts of lead, lime, and barium produce white precipitates.

If tungstic acid is dissolved in the sulphuret of potassium, or of sodium, and an acid is added, the tungstenum is precipitated in the state of sulphuret, of a deep-brown colour, nearly black.

Molybdenum. (Mo 46.)

This metal is obtained in nature combined with sulphur. The ore has much the resemblance of plumbago; but the metal itself is white, resembling silver, and difficult to fuse. It is not soluble in dilute acids, but dissolves readily in *aqua regia*. It combines with oxygen in three proportions—

Protoxide = Mo O.
Peroxide = Mo O_2.
Molybdic acid = Mo O_3.

The protoxide is of a black colour; is difficultly soluble in acids, giving a black solution, not crystallizable.

Peroxide of Molybdenum is obtained by digesting molybdic acid with hydrochloric acid and copper; the solution has a deep-red colour, and by adding to it an excess of ammonia, the copper is dissolved, and the peroxide of molybdenum is precipitated. This oxide dissolves in acids, forming salts which are red when crystallized, owing to the presence of water, but when rendered anhydrous, they become black.

Oxalic acid dissolves this oxide, and forms with it a salt which crystallizes in bluish-black crystals. These crystals are soluble in water, and give a red coloured solution, to which, if ammonia be added, a red-brown precipitate is obtained.

Molybdic Acid is obtained by roasting the native sulphuret in the air until all the sulphur is evolved; the acid remains as a powder. When required pure, this powder is dissolved in ammonia, and the solution is evaporated in order to crystallize the acid. The crystals obtained are then submitted to a moderate heat to drive off the ammonia, and the acid remains pure. It is slightly soluble in water, but combines readily with the alkalis, forming salts, which are all soluble in water, and

all crystallizable. By adding an acid to the solution of these salts, the molybdic acid is precipitated. They act towards re-agents as follows:—

Salts of lead.....White precipitate.
Nitrate of silver .....White precipitate.
Persalts of iron.....Yellow precipitates.

The salts formed by dissolving the peroxide in an acid, act towards re-agents as follows:—

Solution of galls .....Yellow precipitate.
Red prussiate of potash, } Brown precipitates.
Yellow prussiate of potash, }
Potash and soda .....Brownish-black precipitates.
Carbonates of the alkalis.....Light-brown precipitates.
Sulphurets of the alkalis.....Brownish-yellow precipitates.

Similar precipitates may be obtained from the salts of molybdic acid, by adding, along with the re-agents, a little hydrochloric acid, to take up the alkali of the salt.

Tellurium. (Te 64·2.)

This is a metal which is found in combination with silver, bismuth, and lead. Its colour is silver-white, its structure crystalline and brittle; it volatilizes at a high heat, and burns in air with a blue flame. It combines with oxygen in two proportions, both of which have acid properties:—

Tellurous acid = Te_2.
Telluric acid = Te_3.

Tellurous Acid is a light, white, earthy powder, soluble in acids, and also in the alkalis, with which it forms salts, (*tellurites,*) which are very soluble in water, and easily decomposed.

Telluric Acid may be obtained by first fusing tellurous acid with nitre, which gives tellurate of potash; then by dissolving this salt, and adding a solution of barytes, there is formed an insoluble tellurate of barytes, which is again decomposed by digestion in sulphuric acid; the sulphuric acid takes up the barytes, and the telluric acid remains in solution, and may be afterwards crystallized. A tellurate of soda and potash may

be formed by dissolving these alkalis in the acid: they are soluble in water.

The action of re-agents upon the salts of tellurium is as follows:—

Alkalis.....White precipitates, redissolved.
Yellow and red prussiate...No precipitate.
Solution of galls .....Yellowish precipitate.
Sulphuretted alkalis.....Brownish precipitates.

Arsenic. (As 75.)

This metal is very abundantly distributed in nature, and is found in various states of combination. It is chiefly, however, associated with iron, nickel, and cobalt. Arsenic has a grey steel lustre, is brittle, crystalline, and very easily sublimed, rising in vapour at a heat of about 356°, and is thus easily separated from its ores. It combines with oxygen in three different proportions:—First, a greyish oxide, probably suboxide, which forms upon the surface of the metal by exposure to air; and

Arsenious acid = $As\ O_3$.
Arsenic acid = $As\ O_5$.

Arsenious Acid.—This is plentiful in commerce as white oxide of arsenic; it is a heavy white opaque mass as sublimed, although generally sold in the market as a powder and in crystals. This acid is dissolved by boiling water, in the proportion of about 1 part to 10 of water; but on cooling, the solution deposits nearly three-fourths of this quantity. It has little, if any, taste, but is notoriously a deadly poison.*

* The best antidote for arsenic, when taken into the stomach, is newly-precipitated peroxide of iron. This can always be obtained in a very few minutes in the dye-house, by adding to the nitrate, or any other *per*-solutions of iron, a little potash or soda: the iron is immediately precipitated. The precipitate ought first to be washed with water, and then taken in the gelatinous state. The arsenious acid in the stomach receives oxygen from the peroxide of iron, and is converted into arsenic acid, which combines with the protoxide of iron, which is not poisonous. Should arsenic be taken into the stomach in the state of arsenic acid, protoxide of iron will serve the same purpose as the peroxide, and is obtained by precipitating some copperas, by means of an alkali.

It dissolves in hydrochloric acid in much greater quantity than in water, but does not combine with the acid, (see Chlorine.) It is rapidly dissolved in hot solutions of bitartrate of potash, and forms a crystallizable salt.

It is dissolved also in great quantity by solutions of potash and soda, and also, but not so effectually, by the carbonates of these alkalis.

This acid, as before mentioned, (page 171,) is used in the dye-house for dyeing Scheele's green, (*arsenic sages;*) but we are convinced that similar colours might be produced by other means; and there cannot be a doubt but that any process which would supersede its use would benefit all who are engaged in the preparation of such goods. Common humanity, indeed, dictates its complete abandonment as a dye. Nor is the evil so much in the operations of dyeing, as in those that succeed: persons who have occasion to work with the yarns after they are dyed, suffer more severely than the dyers. The colour being merely a precipitate of the arsenite of copper (a most deadly poison) upon the fibre of the yarn, to which much loosely adheres, it is readily disengaged as dust in the dry state, and in the process of winding, especially, much of it is unavoidably inhaled by the unfortunate operative. The result is, as might be expected, that health is seriously impaired, and not unfrequently the consequences are fatal. It is, in fact, consistent with our knowledge, that individuals of this class have never recovered from the effects of winding a quantity of arsenic sage-yarn, for which they were paid *one shilling!* Warpers also are subjected to the same baneful evil, although in a less degree; and even the weaver is not exempt from it. Altogether, indeed, the injury to the community by the use of this dye outweighs a hundredfold that arising from the unrestricted sale of poisons, against which so loud a protest was lately raised. We are convinced, moreover, that it is a gratuitous evil, and that dyers would very soon, under the pressure of a little public opinion, find means of avoiding it, and producing the colour innocuously, and of an innocuous character.

Arsenic Acid.—This acid is made by heating arsenious acid with about its own weight of water, and when at the boiling point adding nitric acid, as long as red fumes are given off: the whole is then evaporated to dryness, to expel any excess

of nitric acid that may be present. The heat of the mass, when dry, must not be high, otherwise the arsenic acid will be decomposed. Arsenic acid is milk-white, deliquesces, and is soluble in water: its solution having a sour taste, and strong acid reactions.

When an equivalent of arsenic acid is ignited with an excess of carbonate of soda or potash, a subsalt is formed, which is soluble in water, and easily crystallized. Salts of the alkalis are also formed by adding arsenic acid to hot solutions. These salts crystallize, and their solutions in water give white precipitates with the solutions of the earths and their salts. Solutions of the salts of lead also give white precipitates; nitrate of silver a precipitate of a brown colour; and salts of copper produce green precipitates. These salts can all be made available in the dye-house, although, for the reasons above stated, it would be well if substitutes were used.

Sulphurets of Arsenic.—There are two compounds of sulphur and arsenic, which are, or rather were, occasionally used in the dye-house. These are—

Realgar = $As S_2$.
Orpiment = $As S_3$.

The first of these can be prepared by fusing arsenic, or arsenious acid, with sulphur; it is transparent, and of a fine ruby colour.

The latter may be prepared by adding to a solution of arsenious acid in hydrochloric acid, a sulphuret of an alkali, either potash or soda; it is precipitated of a rich yellow colour, and is much used in painting under the name of *king's yellow*.

Both of these sulphurets are found native. Their principal use in the dye-house was in the blue vat.

Arsenic combines readily with hydrogen, and forms a gas, *arseniuretted hydrogen*, which is very poisonous. When arsenic is present in any solution from which hydrogen is being given off, arseniuretted hydrogen is formed, and therefore care ought to be taken not to breathe any of the gas. Sulphuric acid (see page 92) often contains arsenic.

Antimony. (Sb 129.)

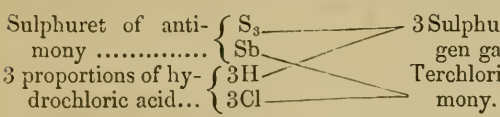
This metal is found in considerable abundance associated

with sulphur, which is separated from it by roasting. Antimony is a bright and white metal, of a crystalline structure, very brittle, and not oxidized by exposure to the air. It volatilizes at a high heat and oxidizes, or burns at a red heat, when exposed to the air: it then passes off in white fumes. Antimony combines with oxygen in three proportions, forming—

Oxide of antimony = $Sb\ O_3$.
Antimonious acid = $Sb\ O_4$.
Antimonic acid = $Sb\ O_5$.

Oxide of Antimony may be prepared either by sublimation, as already stated, or by precipitation from a solution of any of its salts, by an alkali.

When the sulphuret of antimony (the common ore) is digested in strong hydrochloric acid, the metal dissolves, and forms a chloride of antimony, or rather a terchloride, as follows:—


Sulphuret of antimony ..... S3 Sb
3 proportions of hydrochloric acid... 3H 3Cl
3 Sulphuretted hydrogen gas.
Terchloride of antimony.

The clear solution being poured off, and heated to the boiling point, carbonate of potash or soda is then added, and the antimony is precipitated in the state of oxide as a white powder. Both potash and soda dissolve this oxide.

Sulphate of Antimony may be prepared by digesting the sulphuret in strong sulphuric acid with the aid of heat; or the metal may be substituted for the sulphuret.

All the acid salts of antimony are decomposed by aqueous dilution: an insoluble oxychloride is thereby formed and precipitated as a white powder. There are, however, several double salts of antimony with other substances, which are soluble, and not precipitated by dilution. Thus, when a strong solution of binoxalate of potash is heated, and oxide of antimony added, a salt is formed, which is soluble in water, and from which the antimony is not precipitated by dilution. Again, when oxide of antimony is boiled in water, and tartrate of potash added, a double salt (tartar emetic) is formed, which crystallizes, and is not precipitated by dilution.

Antimonious Acid is obtained by oxidating or acting upon, metallic antimony with nitric acid. It is also formed when sulphate of antimony is roasted. Some doubts exist as to the true nature of this compound; it is probably a mixture of oxide of antimony with antimonic acid, (thus $Sb\ O_3 + Sb\ O_5$,) having the same elements as 2 proportions of antimonious acid $= Sb\ O_4$. The combinations of this acid have not been studied.

Antimonic Acid is prepared in the same manner as described for arsenic acid, that is, by acting upon the oxide with nitric acid, and expelling any excess of the acid by heat. Antimonic acid is a pale-yellow powder, not soluble in water, but soluble in potash and soda, with which it forms antimoniates, which, however, are not stable, and are decomposed by almost any other acid or salt.

The precipitates formed by re-agents with salts of antimony are nearly all white, but when a sulphuret of any of the alkalis is added to a solution of antimony, a beautiful golden yellow precipitate is formed.

Uranium (U 60.)

This rare metal is a component of the mineral named pitch-blende, which contains several other metals. Its metallic characteristics have only been recently ascertained; indeed, one of its oxides was, till lately, regarded as an element. It is a white coloured metal very like silver, but is peculiar in being very inflammable, burning with great brightness at a low red heat. It combines with oxygen in several proportions, but only two of its oxides are soluble in acids, and form corresponding salts. These are the

Protoxide $=$ U O.
Peroxide $= U_2\ O_3$.

Protoxide of Uranium is obtained by acting upon the mineral above-named, by *aqua regia*, and separating it from the various other metals with which it is associated, by precipitation. When a solution of uranium in an acid is precipitated by an alkali, and the alkali is well washed out, the remainder is in the state of protoxide. This oxide dissolves with difficulty in hydrochloric acid, but more freely in dilute sulphuric

acid with the aid of heat, and gives a green solution, which yields similarly coloured crystals. It is very soluble in nitric acid, forming a nitrate. These salts give the following reactions:—

Alkalis.....Brownish precipitates.
Carbonates of the alkalis.....Greenish precipitates.
Yellow prussiate of potash ...Reddish-brown precipitate.
Red prussiate of potash .....Reddish-brown precipitate, after a time.
Sulphurets of the alkalis.....Black precipitates.

Peroxide of Uranium is obtained by precipitation from a solution of the mineral by means of an alkali; the precipitate is collected, but the alkali is *not* washed out, and the residue is then exposed to a red heat: the presence of the alkali prevents the metal, which is present as a peroxide, from passing into the protoxide state. When thus treated the oxide is stable. Ammonia, however, will not serve as the precipitant in this case, as on account of its volatile nature it would be dissipated by the heat to which the precipitate must be exposed.

The peroxide of uranium has a beautiful yellow colour, and is soluble in all the acids, and forms persalts. The solutions of these salts act towards re-agents as follows:—

Alkalis and their carbonates...Yellow precipitates.
Yellow prussiate of potash.....Reddish-brown precipitate.
Red prussiate of potash.....No precipitate.
Solution of galls.....Dark brown precipitate.
Sulphurets of the alkalis.....Brown precipitates.

It may be inferred from these reactions, that could this metal be obtained in sufficient quantity, it would form a valuable addition to the dyer's colouring matters. At present, however, it is too scarce to be regarded as of any practical importance.

Cerium (Ce 47.)

This metal is obtained in small quantities from several minerals, found chiefly in Sweden and Greenland. These are acted upon by *aqua regia*, and the metal is separated by re-agents. Hitherto it has been obtained only as a powder

of a brownish-black colour, which is rapidly decomposed in water. With oxygen it forms

Protoxide = Ce O.
Peroxide = $Ce_2 O_3$.

The oxides and salts of cerium are mostly white, but have not been subjected to any close investigation. Re-agents generally give white precipitates with solutions of the salts.

Mercury (Hg 100.)

This metal is found abundantly both in the metallic state and in combination with sulphur, forming the mineral *cinnabar*, from which the metal is distilled, by heating it with iron and lime. Mercury at ordinary temperatures is liquid: hence its popular name of *quicksilver;* it has a high metallic lustre, becomes solid at 40° below zero, and gaseous at 662°. It combines with oxygen in two well-known proportions:—

Suboxide = $Hg_2 O$.
Protoxide = Hg O.

Suboxide of Mercury is a black powder, and is obtained by precipitation from a cold solution of calomel by potash or soda. It dissolves in acids, and forms a series of salts of great use in medicine. The common calomel of the druggists is a subchloride of mercury = $Hg_2 Cl$. The subsalts of mercury give the following reactions:—

Alkalis.....Black precipitates.
Carbonates of the alkalis.....White precipitates, which become black by heating.
Yellow prussiate of potash...White precipitate.
Red prussiate of potash.....Reddish-brown precipitate.
Solution of galls.....Light yellow precipitate.
Bichromate of potash.....Red precipitate.
Sulphurets of the alkalis.....Black precipitates.

Protoxide of Mercury, Peroxide of Mercury.—This oxide is obtained by heating mercury in contact with oxygen, or by exposing nitrate of mercury to heat until all the acid is expelled. Its colour is a deep red, and hence it is known in commerce as *red precipitate.*

When mercury is acted upon by an acid, *persalts* are generally formed. These salts may also be formed by dissolving the red oxide in the acids. Thus the perchloride (*corrosive*

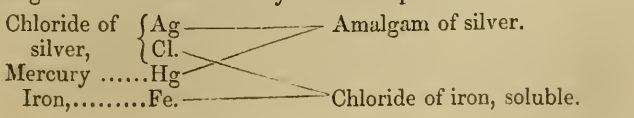
sublimate) may be prepared by dissolving the red oxide in hydrochloric acid. There are a great variety of salts of mercury, nearly all poisonous, and all less or more used in medicine. None of them are used in dyeing, but some are useful as tests. The following are their reactions with other substances:—

Potash and soda.....Yellow precipitates.
Ammonia.....White precipitate.
Carbonates of the alkalis.....Reddish-brown precipitates.
Carbonate of ammonia.....White precipitate.
Yellow prussiate of potash ...White precipitate.
Red prussiate of potash.....Yellow precipitate.
Solution of galls.....No precipitate.
Iodide of potassium.....Red precipitate.
Bichromate of potash.....Red precipitate.
Sulphurets of the alkalis.....Black precipitates.

These colours are not generally permanent upon cotton, but are destroyed when exposed to a moderate heat.

Silver (Ag 108).

This metal is found in considerable abundance in nature, and is very widely diffused: it is generally in combination with sulphur, along with other metals, particularly with lead. It is obtained from the lead ores of this country, and is extracted from them by cupellation, as was described under the head of Litharge, (page 172.) It is also extracted from its sulphurets, and from some other ores which are found abroad, from which the greater quantity of the silver is obtained, by roasting the ore, after mixing with it a quantity of common salt, which converts the silver into a chloride. The ore is next put into large barrels with water and scraps of metallic iron and mercury, and the barrels are kept revolving in order thoroughly to mix their contents. The iron decomposes the chloride of silver, and becomes a chloride of iron, and the mercury takes the liberated silver, and forms with it an amalgam. The reactions may be thus represented:—



The amalgam is collected and subjected to a high heat in a retort; the mercury is thereby distilled over, and the silver remains behind.

Silver is the whitest of all the metals; it is also highly ductile and malleable, and does not combine with oxygen by exposure to the air, but is very soon tarnished by the fumes of sulphur, which always exist to some extent in localities where coal is burned. Silver combines with oxygen in three proportions:—

Suboxide = Ag_2 O.
Protoxide = Ag O.
Peroxide = Ag O_2.

The first and last of these oxides are little known; the protoxide is of the most importance, and is obtained as a deep brown powder, by adding an alkali to the solution of any soluble salt of silver. This oxide dissolves in acids, and forms protosalts.

Nitrate of Silver.—Nitric acid, diluted, dissolves silver by the aid of heat with great ease; and the nitrate formed is the salt commonly used in the laboratories. It is very corrosive, blackens the skin, and constitutes the permanent marking ink for linen, which, by the way, may be easily obliterated by dipping the cloth in chlorine water. The chlorine converts the silver into a chloride, which is washed out by passing the cloth through liquid ammonia.

Sulphate of Silver.—Silver is dissolved by hot sulphuric acid, and forms a sulphate of silver. This salt crystallizes, and is very corrosive, but it is little used.

The attraction of silver for chlorine is so great that hydrochloric acid, or any chloride, added to a salt of silver, instantly decomposes it, and converts the silver into an insoluble chloride. Hence it is that chlorides are the best tests for silver, and that silver is in turn the best test for chlorine.

Oxide of silver is soluble in acetic acid, and many of the milder acids; and several of its salts are now extensively used for photographic purposes.

Chloride of silver is soluble in hyposulphite of soda, forming a salt, which is also much used in obtaining pictures by means of light: the study of the action of light upon these salts is indeed well worthy the attention of dyers, (page 15,) as

the phenomena are highly suggestive of practical application.

When experimenting with salts of silver, it is, of course, important that none of the metal be lost; and it may be all recovered by converting it into chloride, evaporating the solution, and when dry, mixing with three times its weight of dry carbonate of potash; putting this into a crucible, and fusing for fifteen minutes: when the crucible cools, the metallic silver will be found as a button of metal at the bottom.

The salts of silver have the following reactions with other substances:—

Potash and soda	Brown precipitates.
Ammonia	Brown precipitate, very soluble in excess.
Carbonates of the alkalis	White precipitates.
Yellow prussiate of potash	White precipitate.
Red prussiate of potash	Red-brown precipitate.
Solution of galls	No precipitate.
Bichromate of potash	Crimson-red precipitate.
Sulphurets of the alkalis	Black precipitates.

The necessary expense of this metal prevents its introduction to the dye-house; and we are afraid that its property of becoming black by light would destroy its general usefulness even could it be had sufficiently cheap.

GOLD. (Au 197.)

This metal is commonly found in the metallic state, and nearly pure, but sometimes it is associated with other metals; it is extensively diffused through nature. When it is found along with silver, the ore is treated in the same way as the other ores of silver, and the two metals are obtained together in alloy; but when the metal is diffused through the rock, in the metallic state, the rock is stamped to fine powder, and then submitted to a current of water, which carries away the light earthy portion, and the gold falls to the bottom from its superior weight. This residuum is mixed with metallic mercury, to form an amalgam with the gold;

which is afterwards distilled in the same manner as was described for silver.

Gold and silver are separated by subjecting the alloy to nitric or strong sulphuric acid, which dissolves the silver and leaves the gold. The silver is precipitated as a chloride, and reduced, by fusion with carbonate of potash, an operation which is termed parting.

Gold is the only yellow metal known; it is the most ductile as well as the most malleable of the metals, and does not oxidate or tarnish by exposure to the air, which gives it an intrinsic value over most of the other metals. It does not dissolve in any single acid, but is readily acted upon by *aqua regia*, forming a perchloride. It combines with oxygen in two proportions:—

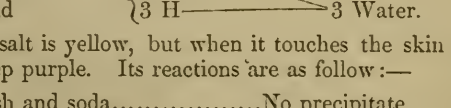
Suboxide = $Au_2 O$.
Peroxide = $Au_2 O_3$.

The first of these oxides is obtained by adding a solution of potash to subchloride of gold: it is a green powder.

The peroxide is obtained by precipitating the solution of gold in *aqua regia* by magnesia, and washing the precipitate by a little nitric acid. This oxide is of a brown colour.

Subchloride of Gold is prepared by evaporating a solution of gold in *aqua regia* to dryness, and heating the residue to about 400°, until all smell of chlorine has ceased, stirring all the while. The product is the subchloride, and is decomposed by water.

Perchloride of Gold.—This is the salt obtained by dissolving the metal in *aqua regia;* but which may be had purer by dissolving the peroxide in hydrochloric acid. Thus:—



This salt is yellow, but when it touches the skin it dyes it of a deep purple. Its reactions are as follow:—

Potash and soda.....No precipitate.
Ammonia .....Yellow precipitate.
Oxalic acid.....Dark-green precipitate.
Yellow prussiate of potash.....Light-green precipitate.

Red prussiate of potash .....No precipitate.
Protosalts of iron .....Brown (metallic gold) precipitates.
Protosalts of tin.....Purple precipitates.
Solution of galls.....Black precipitate, which becomes brown (metallic gold).

Salts of this metal, on account of their expense, can only be used as re-agents in the laboratory, not in manufacturing operations.

Platinum. (Pt 98·7.)

This metal is found in a native state in the *debris* of rocks belonging to the earliest igneous formation. It was first discovered in the auriferous sands of some rivers in America, but is now found in various localities. Platinum is a white metal, very ductile, and also malleable; it is the densest metal known, and is not acted upon by exposure to the air, nor oxidized by heat. No single acid affects it, on which account it is exceedingly useful in many chemical processes. *Aqua regia* dissolves it with the aid of heat, and forms with it a perchloride. It combines with oxygen in two proportions:—

Protoxide = Pt O.
Peroxide = Pt O_2.

The protoxide is obtained by digesting the protochloride in potash; it is a black powder, soluble in excess of potash, yielding a green solution, from which the platinum may be precipitated.

The protochloride is obtained in the same manner as the protochloride of gold; it is a greenish powder, slightly soluble in strong hydrochloric acid.

The peroxide of platinum is obtained by adding to a solution of sulphate of platinum some nitrate of barytes: the sulphuric acid is precipitated, and nitrate of platinum is formed, and remains in solution. By adding to this solution a little soda, peroxide of platinum is precipitated as a reddish-brown powder. This oxide dissolves in acids, forming salts,

which are mostly of a brownish-red colour, and has a strong attraction for the earthy bases.

The sulphate is prepared by adding to a solution of platinum in *aqua regia*, drop by drop, a solution of sulphuret of potassium, which forms a bisulphuret of platinum; by exposure to the air, the sulphur attracts oxygen, and becomes sulphuric acid, which combines with the metal.

Bichloride of platinum is the salt formed when the metal is dissolved in *aqua regia;* it has a deep-red colour. This salt combines with chloride of potassium, and forms with it a double salt, which crystallizes in beautiful reddish-yellow crystals. The persalts of platinum are all more or less red in colour, and have the following reactions with other substances :—

Potash, soda, ammonia, and their carbonates..... } Yellow precipitates.
Yellow prussiate of potash.....Yellow precipitate.
Red prussiate of potash .....Yellow precipitate.
Solution of galls .....No precipitate.
Protochloride of tin.....A reddish-brown coloured solution, the tin being rendered a perchloride, the platinum a protochloride, but there is no precipitate.
Sulphurets of the alkalis.....Reddish-brown precipitates.

Palladium. (Pd 53·3.)

This metal is found associated with platinum; its appearance is very similar, except that it has a slightly reddish tint, and only about half the density. It is nearly as infusible, but its surface slightly tarnishes by exposure to air, and it is soluble in nitric acid. Like platinum, it combines with oxygen in two proportions :—

Protoxide = Pd O.
Peroxide = Pd O_2.

The protoxide is a dark-brown powder, and is obtained by dissolving the metal in nitric acid, evaporating to dryness, and heating the residue to drive off the acid; or it is precipitated from the acid by an alkaline solution.

The protochloride of palladium is formed by dissolving the metal in hydrochloric acid, to which a few drops of nitric acid have been added. The former acid acts upon the metal slowly when alone, but this addition quickens the action. The solution is evaporated to dryness, to expel any excess of acid, and yields a compound of a dark-brown colour, which is protochloride. This salt combines with chloride of potassium and sodium, and forms double salts, which deposit yellow-coloured crystals from their solutions.

The peroxide of palladium is obtained by first dissolving the metal in strong *aqua regia:* this gives a solution of a dark-brown colour, which is a bichloride of the metal. To this solution is added, *gradually*, either potash or soda, which precipitates the metal as a hydrated peroxide of a reddish-brown colour. The salts corresponding to the peroxide are little known. Solutions of the protosalts of palladium act towards re-agents as under:—

Potash and soda	Brownish precipitates.
Ammonia	No precipitate.
Carbonates of potash and soda	Brown precipitates.
Yellow and red prussiates of potash	No precipitates.
Protochloride of tin	Black precipitate.
Phosphate of soda	Brown precipitate.
Sulphurets of the alkalis	Black precipitates.

Iridium. (Ir 99.)

This metal is found combined with platinum, which like palladium, it also resembles in appearance. It is more infusible than platinum, and, if pure, resists the action of all the acids; but when alloyed with platinum, it is soluble in *aqua regia.* It is known to combine with oxygen in four proportions, forming—

Protoxide = Ir O.
Sesquioxide = $Ir_2 O_3$.
Binoxide = $Ir O_2$.
Peroxide = $Ir O_3$.

To all of which there are corresponding chlorides known. The salts of this metal are mostly of a rose colour, and insoluble, or nearly so, in water. They are of no practical value.

Osmium. (Os 99·6.)

This metal is always found associated with iridium in platinum, and is obtained in a pulverulent state. It dissolves, when alone, in strong nitric acid and *aqua regia*—in both cases forming osmic acid. It combines with oxygen in five proportions:—

Protoxide = Os O.
Sesquioxide = Os_2 O_3.
Binoxide = Os O_2.
Peroxide = Os O_3.
Osmic acid = Os O_4.

These oxides are nearly all brown. There are also corresponding chlorides, which are generally coloured.

Rhodium. (R 52·2.)

This is another metal found alloyed with platinum, which it resembles in appearance, but is brittle and hard. If pure, it is not acted upon by any of the acids, but when alloyed with another metal, as with platinum, is readily dissolves in *aqua regia*. Soda precipitates both metals from this solution; but the platinum precipitate is soluble in alcohol, and is thus easily separated. The rhodium in this state is of a beautiful rose colour, and combines with oxygen in two proportions—

Protoxide = R O.
Peroxide = R_2 O_3.

The protoxide has not been isolated: the peroxide is a black powder. The salts are all less or more coloured, and generally give coloured precipitates with re-agents. Rhodium has been introduced into the arts on account of its giving great hardness to metals alloyed with it. It is used for tipping metallic (gold and silver) writing pens, &c.

Lanthanium. (La 48.)

This metal has been but recently discovered in a mineral from which cerium is obtained. Its oxide has a brick-red colour, and dissolves in acids, giving red-coloured salts.

Along with this metal another has been detected by the same discoverer, it is named Didymium, and very much resembles Lanthanium in its chemical properties.

Within these few years discoveries of several other metals have been announced; these are all of course rare, and their properties have not yet undergone any very extensive examination. Their names are

Erbium—Niobium—Norium—Pelopium—Ruthenium—Terbium.

Some of these may yet be found to be peculiar combinations of other known metals, but until that is proved, we must look upon them as metallic elements.

In the preceding sketch of the elements, we have treated very briefly all those which have not yet had any practical application to the art of dyeing, and also those that are rare and expensive. Of those elements, we have noticed merely the features and reactions, which seemed to us best calculated to attract attention, or which might suggest experiments, with a view to their application in the trade. And although many of the metallic elements, which give indications of available properties, are at present too rare to be employed, yet we know not how soon the rarest of them may be discovered in abundance; and it is a law, quite as certain as gravitation itself, that if a demand be created, exertion will follow to satisfy it. When chromium was first discovered, it was considered a rare metal, but, as the demand grew, other ores were found to contain it in great abundance, and so it may be with some of those metals now considered the most rare and the most unlikely ever to become abundant.

MORDANTS.

If the various colouring matters used in dyeing had an affinity for the fibre in its natural state, the process would be very simple: it would only be necessary to make a solution of the dye-drug, and immerse the goods in it to ensure their being dyed. But so far from this being the case, if we except indigo and safflower, there is scarcely a dye-stuff that imparts its own colour to goods; nay, the greater part of the dye-drugs used have so weak an affinity, for cotton goods especially, that they impart no colour sufficiently permanent to deserve the name of a dye. The cause of this is obvious. If, for example, we take a decoction of logwood, the colouring matter is held in solution by the water; by putting a quantity of cotton into this solution the fibres become filled with the coloured solution, but if the cotton has no power to render that colouring matter insoluble within its fibres, it is plain, that by taking out the cotton, and putting it into water, the colouring matter within it will be diffused in the water; in other words, the dye having no attraction for the fibre, is washed out. This primary want of affinity makes dyeing sufficiently intricate, and renders it more dependent upon science; indeed, it is only by the nicest arrangement of a few chemical laws, that the dyer is enabled to turn to advantage the various colouring matters of which he is in possession. When the dyer finds that there is no affinity between the goods and any colouring substance which is put into his possession, he endeavours to find a third substance, which has a mutual attraction for the cloth and colouring matter, so that by combining this substance with the cloth, and then passing the cloth through the dyeing solution, the colouring matter combines with the substance which is upon the goods, and constitutes a dye. This third substance used, which acts as a mediator, combining two inimical bodies, is termed a mordant, from the French *mordre*, to bite, from an idea which the old

dyers had that these substances bit or opened a passage into the fibres of the cloth, giving access to the colour. And although the theory of their action is now changed, the term is still continued, and perhaps further investigation will prove the term applicable.

All the mordants, with one or two exceptions, are found among the metallic oxides. It may be supposed from this that, as metals are the most numerous class of elements, mordants are also very numerous; it is not so, however. In order that the substance may act as a mordant, it must possess certain properties: it must have an attraction for the colouring matter, so as to form with it an insoluble coloured compound; and it must be held easily in solution. It may also have an affinity for the fibre, a tendency to unite with it, but this property is not essentially necessary; only the two first properties are so, and they limit the mordants almost wholly to what are termed the insoluble bases—that is, substances which are not by themselves soluble in water.

The bases or oxides which are in general use as mordants, and which appear to succeed best, are alumina, and the oxides of tin and iron; the two first are colourless, and the peroxide of the latter is a light brown, and imparts to white goods a buff or nankeen colour, which in many cases affects to a considerable extent the colour of the cloth, a circumstance which must also be attended to by the dyer. Indeed, the principal part of all dyeing operations is the proper choice and application of mordants; there being a chemical union between them and the colouring matter, a new substance is formed, not only differing in properties, but differing in colour, from any of the originals, consequently a very little alteration in the strength or quality of a mordant gives a decided alteration in the shade of colour. However, it gives the dyer a much wider field for variety of shades; and at the same time a less number of colouring substances are required; as, for example, logwood alone gives no colour to cotton worthy the name of a dye; yet by the judicious application of a few different kinds of mordants, all the shades from a French white to a violet; from a lavender to a purple; from a blue to a lilac; and from a slate to a black, are obtained from this substance.

Before any chemical union takes place between bodies, they must not only be in contact, but they must be reduced to their

ultimate molecules; hence, mordants that are insoluble of themselves must be dissolved in some appropriate menstrua before their particles can enter the fibres of the goods, or combine with the colouring matter. In doing this, the dyer must attend to the degree of affinity between the solvent and the mordant, to determine what force it will exert against the mordant combining with the fibres of the cloth, should there exist an affinity between them, otherwise a powerful mordant may be weakened by the attraction of its solvent; as, for example, common alum, even though much concentrated, is but a weak mordant for cotton goods, owing to the great attraction between the sulphuric acid and the alumina. But if acetic acid, which has comparatively a weak affinity for the alumina, be substituted for the sulphuric acid, it becomes a very powerful mordant. From these things having to be attended to, the dyer has many beautiful illustrations of the relative attraction of different substances for each other. In some cases the attractions are so nicely balanced that the mordant and colouring matter may be kept mixed, and the goods, when immersed in this solution, having a kind of reciprocal affinity, only receive their share, and do not extract the colouring matter from the solvent, but the depth of colour upon the cloth corresponds with the colour of the solution. In other cases the attraction between the mordant and colouring matter is so powerful, that, if the least quantity of the mordant solution be upon the cloth when put into the dye, it seizes the colouring matter, which is instantly precipitated or rendered insoluble, and therefore unfit to combine with the goods, and what colouring matter may have combined with the cloth before being all precipitated, will be uneven; that is, the resulting colour will be light and dark. From these circumstances, the close alliance of the art of dyeing to the science of chemistry, is evident; but an individual from experience may know these effects, and, though ignorant of the cause, may often guard against their consequences; knowledge, however, procured only by routine practice, is purchased at a very great cost, and attended with many unpleasant circumstances. In cases where the base has no affinity for the fibre, there exists the same difficulty as with the colouring matter, the fibre being filled with the solution of the base; should the goods so filled be passed through water, the base will be washed

out; and should they be put into the dyeing solution, immediately and directly a great quantity of the colouring matter will be precipitated upon the fibre, not within it, and will thus be left merely adhering to the surface, and, when dry, much of it will of course come off as dust, which is so much loss. Thus, the salts of lead have little or no affinity for the fibre, and if cotton, impregnated with nitrate or acetate of lead, be washed several times, nearly the whole lead is dissolved out. If put through the bichromate of potash solution directly from the lead, a great quantity of chromate of lead will fall to the bottom of the tub, and be lost; but by passing the goods from the lead solution through a little lime-water, the lime takes away the acid, the lead is fixed within the fibre as an oxide, and when put into the chrome solution, combines with the chromic acid, and no chromate of lead is precipitated. Nevertheless there are colours that require a little of the free mordant to be added, to bring out the colour. Thus, a piece of cotton passed through red spirits, and then well washed in water, will not lose all the tin. Let the cotton be put into a solution of logwood, this will combine with the base or oxide of tin, and leave the water nearly colourless, giving a reddish-brown colour to the goods, very imperfect, indeed, and not suitable as a dye; but by adding a small quantity of spirits to this exhausted water, and then immersing the dyed cotton again, instantly, the true violet or purple colour is brought up. The substances thus added to the coloured liquor to change and fix the colours are termed *alterants*, and the operation, in the language of the dye-house, *raising*, because it brightens the colour. Alterants and mordants are often spoken of as two distinct substances; but the only distinction is in the mode of applying them. In some instances distinct substances are used. In the process detailed above, a little alum would do as well as the tin; or if a particular bluish shade were wanted, a little pyrolignite of alumina; but in almost all cases the mordant may also be used as the alterant. This shows that in some instances the dye may require some of the acid in the salt, which constituted the mordant, to bring it out, and must be applied after the colour is fixed. If in the above operation the cloth had been passed through the hot logwood solution directly from the spirit tub, the logwood would have been precipitated; and except the decoction had

been very strong, the colour upon the fibre would have been weak and unequal. Other matters are often added as a sort of alterant in some colours, not to affect the required change of the colour, but to take up some substance that may have a tendency to retain the colouring matter, and prevent its uniting with the mordant. Thus it may be necessary with lead mordants, where the acid of the lead is taken away, to add some acid to the chrome solution, to combine with the potash, in order to liberate the chromic acid, and allow it more freely to take the lead. This is particularly the case with Prussian blue. If the goods are washed from the nitrate of iron solution, or passed through an alkali, a little acid must be added to the Prussiate solution, to take the potash, and liberate the prussic acid.

It is with the vegetable colouring matters, however, that the greatest attention must be paid to the many conditions and properties of mordants: some of these may be shortly noticed.

The mordant, or solvent of the base constituting the mordant, should not be capable of injuring or destroying immediately, or by prolonged action, either the colouring matter or the fabric. Thus acids do not serve as mordants, as they generally either destroy the fabric or the colouring matter; and in cases where destructive acids are used, care has to be taken that they are washed off or neutralized before they have had time to act upon the tissue or upon the colour. The principle here stated opens a very wide field of inquiry, embracing the whole range of dyeing operations. The action of bases upon colours, and the condition of those best adapted to give beauty and permanency, are most important subjects, and deserve that we should here consider them a little in detail.

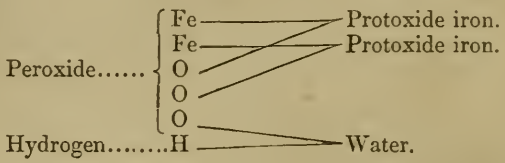
1st. The base being insoluble in water, has to be rendered soluble by combining it with an acid, so as to allow the base to combine with the colouring matter. What becomes of that acid which holds the base in solution when the colouring matter combines with the base? will it act upon the colour formed? We have already discussed this point, as regards lead and chrome, (page 195;) we will now take another colour, which, although strictly speaking it does not embrace the action of a mordant, will serve very well to illustrate the point of inquiry. Indigo is dissolved in strong sulphuric acid

and is used in this state for dyeing green upon light cotton cloths. The goods are first dyed yellow by bark or fustic, and then dyed blue by means of sulphate of indigo, which gives green. Now, were the yellow dye passed through the sulphate of indigo, the acid would destroy the yellow, and spoil the colour; the acid has, therefore, to be neutralized, and soda or potash is employed for this purpose, according to ordinary practice. We have then the sulphate of the alkali held in solution with the indigo; and although the acid will not now destroy the yellow, there is another consideration, namely, the effect of this sulphate of the alkali upon the colour; and if there be an effect, it becomes a question how to avoid it. Thus every circumstance produces a new feature, and should be fully studied.

2d. We must consider the nature and properties of the base constituting the mordant, and its reaction upon the colouring matter, both when combining, and afterwards under exposure. Thus we have stated, when treating of the oxides of iron and tin, that these substances, under various circumstances, are unstable, the protoxide having a strong attraction for oxygen, and the peroxide, when in contact with organic matters, readily yielding oxygen.

In one or other of these conditions, these bases combine with the colouring matter. How, then, will the above properties affect the compound? The action of the peroxide in contact with organic matters, seems to supply an answer to the question, because in all cases in which peroxides give up their oxygen to the organic colouring matter and become protoxides, the protoxide is the proper condition of applying the mordant. On any other supposition it would be necessary to prove that, when peroxide is applied, the giving up of the oxygen produces a reaction favourable to the resulting colour; but this is seldom if ever the case. The reaction of the peroxide is generally the combination of a part of the oxygen with the hydrogen of the colouring matter, which thus becomes partially decomposed. This will be seen by attempting to dye common black with a persalt instead of a protosalt of iron, or by adding a persalt of iron to a solution of galls or sumach, and allowing them to stand, the colour will be greatly deteriorated. Supposing cloth from sumach put into a solution of persulphate of iron, there will be a decomposition: the per-

sulphate being *three* acid and *two* iron, some of the hydrogen of the vegetable colour will produce one proportion of free acid by the reduction of the *per* to the *proto* sulphate. When peroxide of iron is fixed upon the cloth free of acid, and put into the colouring matter, water is formed by the oxygen of the peroxide and colouring matter. We then have—



So that one-third of the colouring matter will be destroyed, and a more imperfect dye will result, as will be more fully illustrated when we come to describe the composition of the vegetable dyes.

It is this principle which prevents the use of many oxides of metals that might otherwise be valuable, such as oxide of silver, mercury, &c., which are easily reduced by organic matters. When any of these bases combine with colouring matters as mordants, they are gradually reduced, and pass into the metallic state, the oxygen taking the hydrogen or the carbon of the colouring matter, and thus the colour fades away. Still this property of giving up oxygen is often of great value in other operations, as in working with substances that require oxidation to give a colour, as in the case of catechu; salts of silver, mercury, &c., would serve the purposes for which copper salts are at present applied to this dye-drug; whereas persalts of iron cannot be used with this substance for oxygenizing purposes, as its protosalt blackens the tannin of the catechu, and affects the production of other shades of colour; but where modified tints are required, iron furnishes the means of obtaining them to a great extent. Thus, by a careful study of the conditions of the mordants, their relations to the colouring matter, the reactions that will take place under all the varied circumstances of application, and what kind of reaction is required to obtain the results sought, the dyer will find his trade easy, interesting, and pleasant. When the mind guides the

hand, labour ceases to be felt either as a curse or degradation.

In connection with mordants, Dr. Bancroft, in his work on the Philosophy of Permanent Colours, arranges all colours in two classes. He says:—

"To me, colouring matters seem to fall naturally under two general classes. The first including those matters which, when put into a state of solution, may be fixed with all the permanency of which they are susceptible, and made fully to exhibit their colours in or upon the dyed substance, without the interposition of any earthy or metallic basis. The colours of the first class I shall call *substantive*, as denoting a thing solid, by or depending only on itself; and colours of the second class I shall call *adjective*, as implying that their lustre and permanency are acquired by their being adjected upon a suitable basis.

"Earthy and metallic substances, when thus interposed, serve not only as a bond of union between the colouring matter and the dyed substance, but they also *modify* as well as fix the colour. Some of them, particularly the oxide of tin and the earth of alum, *exalting* and *giving lustre* to most of the colouring matters with which they are united; whilst others, and especially the oxide of iron, blacken some, and darken almost all such matters, if made to combine with them."*

This clear definition will remove many erroneous impressions of the meaning of these terms, *adjective* and *substantive*. We have often heard an adjective colour defined as one that required to be previously mordanted; but this definition is ambiguous, and seems to ground the distinction more upon the *mode* of dyeing than upon the nature of the colour. Thus, by passing a piece of cotton through alum, and then through a solution of logwood, we produce an adjective colour, having been *previously* mordanted; but if the solutions of the alum and logwood be mixed together, and the piece be passed through this mixture, the same colour is produced. Yet, by the above definition, it would be a substantive colour, not being *previously* mordanted, and not because the colour produced is neither that of the logwood nor of the alum, but of the compound formed between them. Again, if we pass a

* Bancroft on Dyeing, vol. i. page 118. 1813.

piece of cotton through a solution of copperas, and then through lime-water, there is first produced a light-greenish colour, which, by exposure to the air, becomes nankeen or buff; and notwithstanding its thus taking two operations, equivalent to mordanting and dyeing, the colour produced is substantive, being the pure peroxide of iron fixed within the fibre. Another fallacy, we have often heard of identifying substantive and adjective with *fast* and *fugitive*. The impropriety of this application of the term is shown by simply referring to the two colours, indigo blue and safflower pink; both are eminently substantive, yet the one is fast and the other fugitive.

The property which the fibre possesses of fixing portions of the dyestuff within its pores, will have to be often referred to: as it bears a very important relation to mordants. Astringent substances, in combining with the fibres of cotton goods, have a strong relation to this action. A piece of cotton, put into a hot solution of sumach, and remaining in it until cool, there is a quantity of the astringent principle fixed upon the fibre, which no washing will remove. We have seen goods thus treated passed afterwards through all the regular operations of bleaching, and still retaining so much of these substances as was sufficient to impart a black tint on passing them through protosulphate of iron. Hence the astringent matters in many vegetable dyes act a very important part in the dyeing operations. Whether such substances as galls and sumach, which are used only for their astringent principle, may be termed mordants, is a question we need not discuss; but they are essentially necessary for fixing within the fibre such quantities of the metallic base or mordant as are required to give depth and permanency to the colour; and as these astringent matters produce tints with the bases, they give us a wider scope for variety of colour. Thus, if we pass a piece of cotton through a solution of protochloride of tin, and then wash it in water, we will have a great quantity of oxide of tin fixed within the fibre by the operation of washing, (page 180;) and by passing this cloth through a decoction of Brazil-wood, and then *raising* with a little spirits, there is a fine, though not very permanent, rose-red produced. If we pass the cotton through bichloride of tin, and then wash, there is little of oxide of tin fixed; for the bichloride is not decomposed, as the protochlo-

ride is, by water. If, then, it be passed through the Brazil-wood in the same manner as the other, a colour of less depth is produced; but if the cloth be previously steeped in sumach, and be then passed through the tin solution, even the bichloride, the astringent principle of the sumach combines with the tin, and forms an insoluble compound; and there is thus fixed a great quantity of the metallic base, which gives the colour with the Brazil-wood, so that when immersed into the wood decoction, there is obtained a colour of great depth and permanency. But the compound of tin and sumach gives a yellow; thus, therefore, peculiar tints of the colour are obtained, and instead of having a rose colour, a deep rich red, between rose and scarlet, is produced. Thus sumach galls, &c., are extensively used in connection with metallic bases, to fix, modify, and impart depth to colours for which these bases are applied. The nature of these astringent substances will be given under the distinctive names of the matters which contain them.

The strong attraction which animal fabrics, as silks and woollens, have for colouring matters, is well known, and makes the dyeing of these matters more simple than that of cotton. The mordants used are often of a class that does not act the part of mordants in cotton. From this cause, means were sought to impart to cotton something of the property of animal tissues. Thus, in analyzing a piece of silk, there were found—

Composition of Neapolitan silk.....

Fibres of silk	53·37
Gelatine	20·66
Albumen	24·43
Cerin.....	1·39
Fat and resin	·10
Colouring matter.....	·05
	100·00

It was considered that, in all probability, the substances giving the property to silk to imbibe and fix colours more easily than cotton, were such matters as albumen, &c., which might be imparted artificially. This led to the new process of animalizing cotton, as it is termed. Upon this subject we extract from

the *Chemical Gazette*, vol. viii. page 384, an excellent article translated from the *Journ. de Chem. et de Pharm.*, vol. xvii. page 271:—

"When an egg is boiled in a colour-bath, the colour immediately fixes itself to the shell. Egg-shells contain, like bones, an organic tissue and mineral salts. If it is attempted to dye these mineral salts—the phosphate or carbonate of lime—separately, it fails, and therefore neither of these salts can be regarded as the mordant. If, on the contrary, it is attempted to colour the organic tissue of egg-shells or of bones, this immediately becomes dyed; hence it follows that the organic matter of the bones and egg-shells is the mordant.

"Now, in the same manner as mineral mordants have hitherto been employed to fix colouring matters upon cotton, organic mordants may be used, and Broquette has already employed caseine for this purpose. The coating of vegetable fibres with animal substances was first carried out by M. Hausmann, as observed by M. Barreswil, in this article; but is said never to have attained to any importance. The caseine must, of course, be first dissolved, in order that the tissues may be permeated by the solution, but it must then be rendered insoluble in the tissues. Now it has been shown by Braconnot that caseine furnishes a soluble compound with ammonia, which is again decomposed by boiling. Broquette, therefore, impregnates the goods with a solution of caseine in ammonia, then heats them to expel the ammonia, upon which the caseine remains in an insoluble state in the tissues.

"Cotton goods, after this treatment, are saturated with animal matter, and may now be dyed in the same colour-baths as those used for woollen tissues.

"Frequently the dyes are alkaline; they then dissolve the caseine, instead of being fixed by it. But since Bachelier used as a cement a mixture of lime and caseine, it is known that this mixture hardens and becomes fixed. Broquette therefore employs the caseine sometimes with lime alone, sometimes with ammonia and lime together, and saturates the goods with this caseate of lime, which soon sets in a warm atmosphere, and then resists the alkalis and rinsing with alkaline liquids.

"By this treatment, the cotton acquires a peculiar stiffness; so that although its capacity for dyes has become nearly equal

to that of wool, it is far behind the latter, owing to want of lustre. But this evil can also be remedied by mixing the mordant with oil. Oil, caseine, and lime, form a mordant which fixes the colours with a perfectly remarkable lustre.

"When the goods to be dyed consist of wool and cotton, a different plan has to be followed; the mordant in this case is not adapted for the two materials; the wool is deprived of its natural lustre, and the cotton tissues are not sufficiently penetrated. For such goods Broquette employs the mordant before the weaving; it is applied to the cotton in the spinning, when it can afterwards be woven and bleached like wool, without the mordant experiencing any injury. When threads thus prepared are woven, the tissues can be dyed just like woollen stuffs, without further treatment.

"By means of the solution of caseate of lime, mineral colours which are insoluble in water can be adapted to the dyeing of stuffs; they are mixed in a state of very fine powder with the solution. These liquid colours, which can be prepared, for instance, with ultramarine, ochre, &c., can again be removed with water, unless they have been dried; but as soon as they coagulate, they adhere firmly to the tissues inclosing the colouring principle.

"A further application of the mordant of caseine, oil, and lime, is in the printing of stuffs; in this case we are not limited merely to mineral colours, which by its aid may be fixed upon the goods, but the numerous vegetable colours may be likewise very well applied, by first converting them into lakes by means of alumina or protoxide of tin, and then using these lakes in the same manner as the powdered mineral colours. After being printed, the goods are wrapped in moist linen, and left for about half an hour in the moist vapour in a warm atmosphere. During this time the impressed colour does not dry superficially, but is absorbed into the interior of the fibres, and is then completely fixed in the subsequent drying.

"This new method of mordanting has already had considerable influence upon several pigments, for instance upon archil, which has only been used for dyeing exceptionally; according to Broquette's process, some very beautiful colours are obtained from it, modifications of the peculiar colour of the archil by lime.

"It will be evident, from what has been above stated, that

in this process of dyeing it is requisite to pass the goods through a lime-bath, which will not do for many dyes, as the colours have their tints altered by such treatment. In such cases magnesia is to be substituted for the lime.

"When goods are printed with the mineral colours or lakes, according to the above process, very full colours are obtained, which, in the case of many patterns, is not desirable. To bring out the shades and half-colours in the full-coloured impressions, the printed goods are placed with their coloured surface upon an absorbing ground, cotton stuff, and the forms pressed on the back. The printed portion pressed upon the absorbing surface is deprived of some of its colour, and numerous patterns can be produced in this manner."

The preparation of the salts which constitute mordants has been given under the particular element constituting the base of the salt; but we mentioned that different methods of preparing such salts are practised by different dyers, every one preferring his own method, from some real or supposed peculiarity or advantage it possesses; although in some cases this difference is difficult to appreciate, both because the acids used are not regularly tested, and also because it is a common custom to take the acids by measure; so that when a dyer says he prefers 4 to 1, he as often means 4 jugs as 4 lbs. Now, nitric acid being nearly double the specific gravity of hydrochloric acid, 4 measures of this acid to 1 of nitric acid will be in weight about 2 lbs. hydrochloric to 1 lb. nitric acid. The proportions given in the following recipes are by weight:—

Red Spirits.—These are named from being used in dyeing red by means of Brazil and other red woods. They are sometimes termed *nitro-muriate of tin*, from being prepared by a mixture of these acids. Mix together

1 lb. Nitric acid,
3 lbs. Hydrochloric acid.

Add feathered tin, in small quantities at a time, until the acid ceases to dissolve more; pour off the clear, and preserve in a dark cool place. This is a spirit for a deep heavy red.

If a red of a bluer or crimson hue be required, then—

1 lb. Nitric acid,
5 lbs. Hydrochloric acid,

dissolving the tin as above, will be a better quality of mordant. The proportion of nitric acid gives brown or depth to the red; but some sorts of woods contain more of the yellow or *browning* principle than others. Attention ought to be paid to this circumstance, and to prepare the spirits suitably to the character of the wood which is to be used as the dye. This difference of tints is occasionally regulated by the quantity of tin dissolved; hence some dyers give a definite quantity of tin, generally from 2 ounces to $2\frac{1}{2}$ ounces to the pound of mixed acids: this is, indeed, not far from what is generally dissolved when tin is added to saturate the acid. Whichever method is adopted, it is necessary that there should always be a knowledge of the quantity of tin which the spirit contains; and, moreover, as this is commonly prepared in the open air, the quantity of tin dissolved will depend somewhat on the season of the year, on account of the influence which temperature has on the action of the acid. When red spirits are used with logwood, the influence of the proportions of nitric acid is very apparent, causing the purples, or such colours dyed, to dry brownish—a result which the dyer is often called upon to obtain or avoid. The spirit tub in which the yarn is wrought should stand from 2° to $2\frac{1}{2}$° Twaddell.

Barwood Spirits.—These are named from being used as the mordant for dyeing with that wood. They are prepared by

1 lb. Nitric acid,
6 lbs. Hydrochloric acid,

adding gradually, as dissolved, $1\frac{1}{2}$ ounce of tin to the pound of the mixture; or—

1 Nitric acid,
4 Hydrochloric acid,
2 oz. of tin per lb.

This spirit should not be used within at least twelve hours after its preparation. There are also other variations in the preparation of this spirit; they vary generally from 4 to 7 hydrochloric acid. Excess of tin in this mordant is avoided. The same principle regulates the tint more or less. Nitric acid gives the red a brown or crimson hue. The working solution is $2\frac{1}{2}$° Twaddell; but this dye requires some experience and attention to manage it well.

Plumb Spirits, so called from being used with a decoction of logwood to prepare a dye solution of a deep wine or plumb colour, sometimes termed a *French tub*—

7 lbs. Hydrochloric acid,
1 lb. Nitric acid,

adding by degrees, as dissolved, 1½ ounces tin to the pound of mixture; or,

1 Nitric acid,
5 Hydrochloric,
1¼ ounce tin to the pound of acid.

Some prepare it by dissolving the tin in hydrochloric acid alone. In that case, the vessel containing the acid should be placed in a hot situation; it is generally, indeed, placed in another vessel containing boiling water. The spirits are also prepared by dissolving some of the salts of tin in hydrochloric acid. For 1½ to 2 lbs. of logwood used, 1 lb. of the spirits is added.

Yellow Spirits, as before mentioned, (page 187,) were prepared with sulphuric instead of nitric acid, but they are not now used.

The above embraces, with very little modification, almost all the qualities of spirits used for cotton. That termed oxymuriate of tin, used often for woollens and silks, is prepared by adding to a solution of the salts of tin in hydrochloric acid, some nitric acid, which causes effervescence, and an escape of red fumes of nitrous oxide, in consequence of the peroxidizing of the tin. The same result is often observed in the preparation of the spirits named above, when the tin is added too rapidly, and heat is developed; there is then a rapid solution, and fumes of nitrous oxide are given off, producing what the dyers call *fireing*. Fired spirits, or spirits thus peroxidized, give brownish, dull, and unsatisfactory colours.

Several qualities of spirits are used for woollen and also for silk, by adding salammoniac, or common salt, to nitric acid, along with the tin—the former most commonly, by this method a double salt of chloride of tin and ammonia is produced. The proportions of the acid and the salammoniac and tin are also varied for different objects; but spirits prepared in this way are seldom if ever used for cotton.

Nitrate of Iron is prepared by taking a quantity of nitric acid, and adding clean iron (generally old hoops with the rust beaten off) as long as the metal will dissolve. The acid is best to be diluted in the proportion of about one part to six of water; and after it has ceased to act upon the iron, all the metal not dissolved ought to be removed, otherwise the nitrate will continue to dissolve more of it, and precipitate oxide of iron, and thereby produce a thick insoluble mass at the bottom, (see page 159.) Some prefer to add only a small quantity of iron for light shades, but we have never seen any advantage in such a mode of proceeding. The iron and nitric acid ought, however, to be weighed, and have a fixed relation to each other. This solution of iron should be kept in the dark.

Nitric acid, mixed with much sulphuric or muriatic acid, does not answer well for this solution, as the salts of these acids being crystallizable, require more water than the acids generally have to hold them in solution. Hence the presence of these acids in quantity may cause a confused crystalline mass to be formed at the bottom of the vessel in which the iron is dissolved. But the small quantities of these acids, often present in commercial nitric acid, are not of material importance.

Acetate of Iron and Alumina.—This mordant is now seldom used; but it is useful for dyeing wine colours, &c., with logwood. It is prepared by dissolving equal parts of copperas and alum in boiling water, then adding a solution of acetate of lead as long as a precipitate is formed. Allowing this to settle, the clear solution is the double acetate. But a better and cheaper mode of preparing is to mix *black iron* and *red liquor* together, which form the mordant in question.

Acetate of Alumina, or *Pyrolignite of Alumina*, (see page 143 for an account of its preparation, and the mode of testing it.) It is not, however, prepared by the dyer. We may mention, as this mordant is often dried upon the cloth in stoves at a high heat, that care should be taken not to allow two pieces of the cloth to hang too closely together, which prevents a free circulation of air; nor ought the stove to be too close, otherwise the warm vapour of the acetic acid will react upon the mordant in the cloth, and give an unequal dye, full of dark parts, thus rendering the colour cloudy.

Black Iron Liquor.—This is pyrolignite of iron prepared by

allowing iron to steep in pyroligneous acid. It is not prepared by the dyer. We have given a method also of testing it, (page 159.)

Iron and Tin for Royal Blue.—This is not prepared to stand in reserve, but only when about to be used. The iron used for this colour should be well *killed*, that is, the acid should be well saturated with iron, and produce a solution of a deep dark red. Some dyers add a little muriatic acid to the iron when it is to be used along with the tin. The crystals of tin should be added to the iron liquor immediately before entering the goods, and the liquor should be well stirred to prevent inequality.

Acetate of Copper.—This is sometimes prepared in the dyehouse in the same manner as acetate of alumina, viz., by adding to a hot solution of sulphate of copper (*blue-stone*) a solution of acetate of lead: the clear liquor is acetate of copper. It is better, however, to purchase it in the crystallized state; this forms a good alterant for logwood blues, but it is not much used in cotton dyeing.

Bichromate of potash has of late been introduced as a mordant for cotton with considerable success, especially in mixed fabrics of cotton and wool.

There are a variety of other mordants used in woollen and silk dyeing, but these we do not particularize here, but proceed to enumerate a few theoretical considerations concerning the action of mordants generally, upon silk, cotton, or wool.

Cream of tartar, or bitartrate of potash, is a very feeble mordant alone, still it is universally employed in dyeing woollen fabrics. When used along with alum, sulphate of iron, or chloride of tin, it is a strong mordant, probably owing to decomposition: the sulphuric acid of the alum and iron, and the chlorine with the tin, may take the potash from the tartar, and the alumina, iron, or tin, be converted into a tartrate, and in that state combine more readily with the wool, and be much less destructive of the fabric. Woollen goods seem to require certain thermal and acid conditions of the mordant; and it is known that a portion of the wool dissolves, and an equivalent of the mordant takes its place: this has been especially demonstrated of alum mordants.

For silk, the alum mordant is always used cold, otherwise the lustre of the silk is destroyed; and alum, having the least

quantity of acid, is the best and most effective mordant. This explains why the Roman alum is always preferred. It may also be remarked that silk, in relation to alum, comes closest to cotton.

We copy the following theory of the action of mordants, by M. Dumas, from the *Pharmaceutical Times*, (vol. ii. p. 63):—

"Cream of tartar, or bitartrate of potash, constitutes by itself a feeble mordant, but which is very often used in dyeing light woollen stuffs, to which we may wish to give a delicate but brilliant shade. It is also employed in the dyeing of ordinary woollen goods, but here it is associated with alum, sulphate of iron, chloride of tin, &c. Its influence, under these circumstances, consists evidently in determining a double decomposition, from which we have produced a sulphate of potash or chloride of potassium, whilst the tartaric acid combines with the alumina, the peroxide of iron, or the oxide of tin. Now, it is very probable that the colouring matters remove the alumina, the peroxide of iron, or the oxide of tin, more readily from tartaric than from sulphuric acid. Moreover, the presence of free sulphuric acid would certainly prove injurious, as well to the stuff as to the colouring matter, whilst free tartaric acid can exercise no unfavourable action over them.

"The operation of subjecting wool to the alum mordant is always effected at the boiling point; the mixture used in this process is a compound of alum and of cream of tartar. One of the objects of this addition is to free the bath of the carbonate of lime which the water generally retains in solution, and which, acting on the alum, would determine its partial decomposition by producing an insoluble subsulphate of alumina and potash, and this accumulating on the stuff, and becoming unequally fixed upon its surface, would lead to stains or blotches on passing the material through the dye-bath. But, independently of the above effect, which might be produced by any acid, cream of tartar appears to be capable of effecting a further object, by inducing a double decomposition, which transforms the alum into a tartrate of alumina. However this may be, after one or two hours' boiling in the alum-bath, the cloth, which should be constantly agitated so as to cause a more equal application of the mordant, is withdrawn from the copper, and, after thoroughly

draining, it should be put aside for two or three days, when we wish to dye it with any full-bodied colour. Experience has proved that this repose after the use of the mordant greatly favours the union of the latter with the stuff. In applying the tin mordants we also make use of cream of tartar. It is, moreover, an indispensable addition where we desire to fix the salts of iron previously to dyeing in black.

"Woollen cloth, on being dipped into a cold aqueous solution of alum, appropriates to itself a part of this salt, but without undergoing any very sensible alteration. MM. Thenard and Roard have, indeed, proved that cloth, when thus treated by a cold solution of alum, gives up this salt to boiling water, and that, after a few washings performed at the boiling point, it will have parted with the whole of the alum which it had received in the cold bath. When, however, cloth is boiled in a solution of alum, it yields to this liquid a portion of its organic matter, which becomes dissolved; but, at the same time, it absorbs an equal amount of the alum.

"We have now merely to show the action which wool undergoes when brought into contact with alum and cream of tartar at one and the same time. It is very possible that there may be in this case a simultaneous fixation of alum, as well as of the double tartrate of alumina and potash, and of tartaric acid. The presence of alum in the cloth when taken from the boiling solution is very evident; that of the tartrate of alumina and potash and of free tartaric acid is only presumable.

"Silk, in like manner, unites itself with alum when placed in a cold solution of this salt, and afterwards parts with it to boiling water; it may be reproduced from this liquor by evaporation. The action of silk on acetate of alumina is identical with that of wool. It at first absorbs this salt in its pure form; then by desiccation it loses some acetic acid, and retains a mixture of the acetate together with alumina in its free state; it gives up a further portion of this acetate to boiling water.

"The alum mordant is always used cold with silk; if employed hot, it would destroy its lustre. The bath should not contain cream of tartar when it is intended for this material; on the contrary, we here have recourse to a variety of alum of as neutral a character as possible.

"The theory of the action of mordants is connected in the closest manner with that of dyeing. It may, in fact, be viewed under two very different aspects. Sometimes we admit that there exists a true combination between the stuff and the colouring matter—a combination which can only be determined by a veritable affinity between these two bodies, and which will present a condition analogous to that which occurs in all chemical combinations; that is to say, a state of saturation, beyond which the union of these bodies becomes of a very unstable character; at other times, on the contrary, we regard the dyeing of stuffs as produced by a nearly mechanical phenomenon, by virtue of which the colouring matters become imprisoned in the meshes of the organic filaments contained in the material to be dyed. This latter opinion is evidently the better founded. It approximates the theory of dyeing to some analogous phenomena which we find manifested by animal charcoal on coloured solutions; for, as the animal charcoal seizes upon the colouring matters contained in an aqueous solution, and renders them insoluable by fixing them in a purely mechanical manner within its own pores: so may the wool, the silk, and the cotton, appropriate the colouring matters held in solution, and, by fixing them in their pores, render them more or less insoluble to water. Experience, however, shows that dyeing thus produced is wanting both in intensity and in fixity—two qualities which it derives by the previous application of a mordant. Now, we can readily see that the mordants themselves may become fixed in the tissues by similar causes to those which determine the fixation of the colouring matters by animal charcoal. We know, in fact, that this latter body possesses the property of removing from water not only the colouring matters, but also certain salts. There will, therefore, be no difficulty in imagining that silk, wool, and cotton may, in their character of porous bodies, purely and simply seize upon the alum, and that this salt, when once imprisoned in the meshes of the tissue, may, subsequently, react upon the colouring matter according as this latter, in its turn, penetrates the interior of these materials.

"We may then refer the phenomena of absorption, which characterize the fixation of the mordants and the penetration of the colouring principles into the tissues, to the same cause as

that which determines the action of animal charcoal on certain soluble salts and colouring matters. But, if one of these stuffs be impregnated with alum and then dipped in a bath of soluble colouring matter, it acquires a very deep tint, which appears to be essentially produced by a kind of lac, formed by means of the colouring matter and the base of the mordant. On the other hand, in a great number of cases, the mixture of the above mordant with the dye-bath fails in producing an insoluble precipitate. Thus, when we mix together alum and a decoction of Brazil-wood, no precipitate is formed; and, to obtain a lac from this liquor, we are obliged to add some alkali or alkaline carbonate, such as ammonia; in a word, we must render the alumina free. While admitting, then, in accordance with the experiments of MM. Thenard and Roard, that the stuffs fix the alum in its natural state, we must acknowledge, at the same time, that, by some special action, the tissue subsequently determines the union of the base of the mordant with the colouring matter. This special action is equivalent to that of the alkali.

"Now, it is certain that the above-mentioned stuffs possess, in a high degree, the faculty of seizing upon the insoluble colouring matters when these are presented to them in their nascent state. It is thus that cotton becomes dyed of a rose colour in a liquor which contains carthamic acid in suspension, arising from the decomposition of carthamate of soda by an acid. In like manner we find wool acquire a black colour, when placed in a boiling solution of a salt of iron and tannin, by attracting to itself the black precipitate resulting from their admixture. Consequently, although the dyer generally endeavours to produce the insoluble compound, on which the colouring of the stuff depends, within the very pores of the tissue, still we may affirm that, in many cases, the cloth or other material, when placed in presence of the nascent precipitate, has the property of seizing upon it, and thus acquiring a shade of greater or less intensity.

"It is to this property (which is due to some hitherto undetermined cause) that we must undoubtedly refer the reaction which takes place between the alum and the soluble colouring matters, as well as some of those more mysterious phenomena which are manifested in dyeing. How else, indeed, are we to account for the fact that wool so readily takes a scarlet colour,

while cotton and silk are unable to fix it? How explain the cause of wool so easily appropriating the black precipitate formed by tannin and the salts of iron, while silk, under the same circumstances, acquires a black colour only by great trouble and expense? How, in one word, can we understand why certain colours should fix themselves better on certain materials than on others, unless it be by virtue of some special action, wrongly designated by the name of affinity, but which does not the less constitute a force, or rather a consequence of diverse forces of which we must take full account during the operations of dyeing? To confound, in fact, a chemical affinity properly so called, such as is evidenced in ordinary chemical combinations when produced in definite proportions, with the phenomena of dyeing, is certainly to mix together two very distinct ideas. The union of silk with prussian blue, or of wool with indigo, is quite a different thing to the combination of sulphur with lead. But to consider the tissue as a simple filter, capable of retaining in its pores certain precipitates, and of receiving from them peculiar colours, is to go equally far in an opposite direction; nor would this supposition at all explain the mode in which the coloured lac is formed in most of the operations of dyeing, operations which are effected by an aluminous salt and a colouring bath, altogether incapable of producing any lac, except by the addition of an alkali for the purpose of setting the alumina at liberty, or of a stuff which has the power of taking up the lac, as quickly as it is formed.

"Among the reasons which induce us to regard the insoluble colouring matters and the stuffs as capable of uniting together by virtue of some special force, we must mention the facts elicited by the recent experiments of M. Chevreul, who has found that the stuffs and colours, when once united, form products which are endowed with properties differing, according to the nature of the stuff, in the same given colour. The properties of the dyeing matter are, then, greatly modified by the peculiar action of the tissue on the dye. Numerous examples place the truth of this assertion beyond all question. It becomes, therefore, perfectly clear that it is only by an attentive and systematic study of the specific properties of the stuffs, in their relation to the various dyeing matters which we may desire to fix upon them, that we can hope to direct the future progress of the art of dyeing."

VEGETABLE MATTERS

USED IN DYEING.

INTRODUCTORY REMARKS.

In entering upon this division of our subject, we may mention that it is not our intention to go through a systematic course of vegetable chemistry, but to confine ourselves to those vegetable substances which are used in dyeing, giving their composition and reactions with bases and other matters used in the dye-house. We may, however, give in a few introductory remarks, a general outline of the nature of vegetable bodies. Let us then begin with the consideration of the chemical changes which are supposed to take place in nature, under the influence of light, giving rise to the various colours presented to us in the vegetable kingdom, which will probably aid us in describing the artificial means of imitating nature in these colours, although as yet there is comparatively little known concerning the nature of these changes. For a long time chemists considered iron to be the colouring principle of all animals and vegetables, being almost universally diffused, and capable of assuming a variety of colours either as oxides or solutions; but it was afterwards demonstrated that the iron present in any vegetable, even in those where it existed most abundantly, was altogether inadequate to produce the splendid colours which vegetables assume. Several other hypotheses were proposed to account for the colours of vegetables; but these hypotheses, not being founded upon inquiry and proof, died at their birth. It is only within these few years that the true method of ascertaining the nature and cause of vegetable colours has been adopted; that is, by the ultimate analysis of vegetable substances in all their stages of existence; and since then, a number of important facts have been made known respecting this interesting subject, and new ones are

daily being added; and we hope that these discoveries will be speedily made available to the practical man.

The principal elements of vegetable substances are oxygen, hydrogen, carbon, and nitrogen: the last exists in such a minute quantity, that in many cases it is scarcely appreciable; but according to the opinion of Liebig, who stands at the head of this department of chemistry, it is never absent. It is to be remarked, however, that none of the colouring matters of the dye-woods contain nitrogen. There is also a variety of earthy substances in vegetables, such as lime, iron, magnesia, soda, potash, &c.; but the whole of these never exist in the same vegetable—some of them seem indispensable to the existence of a plant; but they differ according to the nature of the plant, and the soil on which it grows. The three elements, oxygen, hydrogen, and carbon, enter very abundantly into the composition of vegetables, forming from 95 to 99 per cent.; but it must not be supposed from this, that all vegetables are alike in their chemical properties; they may be, and are more varied than the mineral kingdom, considering the few elements which compose them, and are beautifully illustrative of the law of definite compounds (page 21). The following table, showing the composition of a few substances which constitute the great mass of all vegetables, will serve to illustrate this point:—

	Carbon.	Oxygen.	Hydrogen.
Woody fibre	15	10	10
Gum	12	11	11
Starch	12	10	10
Sugar	12	11	11

It will be observed from the table how little change is necessary to produce an entirely different compound. It will also be observed, that gum and sugar are the same in composition, which at first sight appears to contradict the law of definite compounds; but in analyzing substances such as are named in the table, they are reduced to their elements, and, although we obtain the same weight of elements, we have no positive information how these elements may have been united together in the plant. All those bodies which differ in properties, and at the same time give the same number and weight of elements, are termed *isomeric*, signifying *equal parts*. The discovery of bodies having the same number of elements,

and differing in their chemical properties, excited much interest among chemists, and has led to much careful study and investigation; the result has been rather unfavourable to the doctrine of isomerism: there are substances which our neighbours on the other side of the water would designate the *same* with a *difference*—the difference is supposed to be in the numerical arrangement of the elements. As, for example, hydrogen and carbon will combine in the proportion of two and two, four and four, and eight and eight, forming three substances, differing considerably in chemical properties, although the elements are combined in the same relation; but, interesting as this subject is, we cannot in the meantime enter into any lengthened details—it shows us, however, the extensive means employed by nature for giving us a variety of substances. Another point to be observed from the above table is, that the oxygen and hydrogen in each of these compounds are in the same proportion, or in that relative proportion in which they unite to form water. Now, it may be stated as a general rule, that when oxygen and hydrogen are united to carbon, in the proportion in which they form water, the resulting compounds are of a saccharine or mucilaginous character; and when vegetable compounds have hydrogen united to carbon without oxygen, or when there is less of that element than would be required to convert the hydrogen present into water, the resulting compounds are generally oily, resinous, or alcoholic. A table of the composition of a few of these substances will illustrate this:—

	Carbon.	Hydrogen.	Oxygen.
Oil of turpentine	10	8	
Oil of potatoes	5	6	1
Oil of cloves	23	14	5
Resin of gambouge.....	20	14	5
Caoutchouc	4	4	
Bees' wax	37	39	2
Pyroxilic spirit.....	2	4	2
Alcohol	2	3	1

When the proportion of oxygen united to carbon is in greater quantity than the hydrogen, or when no hydrogen is present, the resulting compounds have generally an acid character: green fruits are in this state, which gives

them their sour taste, and makes them deleterious to health, either by giving too much acid to the stomach, or the acid being of a directly poisonous nature; but as the fruit ripens, it takes in or assimilates more hydrogen, and the acid, or at least part of the acid, is converted into a saccharine compound. The following table will show the composition of a few of the most common acids found in vegetables:—

	Carbon.	Oxygen.	Hydrogen.
Acetic acid (vinegar)	4	3	3
Tartaric acid	4	5	2
Citric acid (lemon juice)	4	4	2
Gallic acid	7	5	3
Tannic acid	18	12	8

There are also a number of alkalis, alkaloids or bases, formed in plants, which unite with the acids, constituting a very important feature in the study of vegetable chemistry, but which we will not in the meantime enter upon further than to state that they almost all contain nitrogen as an ingredient.

These being the nature and composition of the principal vegetable compounds, we shall now inquire into the cause of their assuming certain colours, and the effects which acids have upon these colours.

In our remarks upon light, (page 11,) we mentioned that colours depend wholly upon the reflection and absorption of light, by the apparently coloured substance; but it was also mentioned, that this result depends upon the chemical constitution of the particular substance; hence, the inquiry into the cause of vegetable colours becomes a chemical one; and, from the chemical laws above described, these colours must have a definite constitution; and when any change of colour takes place, there must also be a change of chemical constitution. In prosecuting this inquiry, or rather, in collecting the inquiries of the most eminent chemists upon this subject, we shall begin with the paramount colour of the vegetable kingdom, namely, green.

Green is well known to be a compound colour, produced by yellow and blue, and is always produced upon cloth by dyeing it first the one colour, and then the other. It is not always the yellow that is dyed first, according to the description in chemical books; but sometimes the blue, according to

the nature of the dyeing agent, which will be explained in its proper place. Speaking of vegetable green, Berthollet says, "the green of plants is undoubtedly produced by a homogeneous substance, in the same way as the greater number of hues which exist in nature. This colour owes, then, its origin sometimes to simple rays, and sometimes to a union of different rays; and some other colours are in the same predicament. Were the green of plants due to two substances, one of which is yellow and the other blue, it would be extraordinary if we could not separate them, or at least change their proportions by some solvent." This idea of Berthollet, that the green of plants is a distinct substance, existing in the plant, has since been verified. It is obtained by bruising green leaves into a pulp with water, pressing out all the liquid, and boiling the dry pulp in alcohol: when the alcohol is evaporated, there remains a deep green matter, which, by digesting in water, is dissolved, and freed from a little brown-colouring matter with which it was mixed. This substance has been named *chlorophyllite.* The formation of the chlorophyllite seems to depend entirely upon the action of the solar rays. "It is known that the function of the leaves, and other green parts of plants, is to absorb carbonic acid, and, with the aid of light and moisture, to appropriate its carbon. These processes are continually in operation: they commence with the formation of the leaves, and do not cease with their perfect development." But when light is absent, or, during the night, the decomposition of carbonic acid does not proceed: it is evident then that a plant kept always excluded from the light, must have a difference in its composition. "No one can have failed to observe the difference between vegetables thriving in the full enjoyment of light, and those which grow in obscure situations, or which are entirely deprived of its agency: the former are of brilliant tints; the latter dingy and white. Numerous familiar instances might be cited, especially among our esculent vegetables: the shoots of a potato produced in a dark cellar are white, straggling, and differently formed from those which the plant exhibits under its usual circumstances of growth. Celery is cultivated for the table by carefully excluding the influence of light upon its stem: this is effected by heaping the soil upon it, so as entirely to screen it from the solar rays; but if suffered to grow in the ordinary way, it soon

alters its aspect, throws out abundant shoots and leaves, and, instead of remaining white and of little taste, acquires a deep-green colour, and a peculiarly bitter and nauseous flavour. The heart of the common cabbage is another illustration, and the rosy-coloured aspect of the sides of fruit is referable to the same cause. Changes yet more remarkable have been discovered in plants vegetating entirely without exposure to light. In visiting a coal-pit, Professor Robinson found a plant with a large white foliage, the form and appearance of which were quite new to him: it was left at the mouth of the pit, when the subterranean leaves died away, and common tansy sprung from the roots."*

Some very curious and interesting results have been obtained by Mr. Hunt, and others, respecting the effects of the different rays of light upon vegetable substances, all going to prove the great influence exerted by that agent over the vegetable kingdom, and that to it we are indebted for the beauty of our fields and gardens.

From these facts we see that the green colour of vegetables is owing to a peculiar approximate element existing in the vegetable, not invariably, nor altogether essential to the plant, but depending upon circumstances; these circumstances being at the same time the best for the health and existence of the plant. This colour differs from the other colours of vegetables in the time of its appearing. Flowers of plants do not appear till the plant has reached a certain state of maturity; but whenever a plant rises above the soil, it immediately begins to assume the green hue, and this hue is continued till the object of the leaves is completed. When a *chemical change takes place*, the green passes away, and another colour, reddish-yellow, takes its place. These changes are effected in different degrees, and in different lengths of time, just according as the leaves have the property of *absorbing oxygen gas*. Those leaves which continue longest green absorb oxygen slowest. The leaves of the holly will only absorb a small fraction of oxygen, in the same time that the leaves of the poplar and beech will absorb eight or nine times their bulk. These last are remarkable for the rapidity and ease with which the colour of their leaves changes. That leaves do absorb oxygen gas when they change colour in autumn, and

* Brande's Manual of Chemistry.

that it is owing to the absorption of this gas, may be verified by placing some green leaves of the poplar, the beech, and the holly under the receiver of an air-pump, and dry them thoroughly, keeping them excluded from light; when taken out, wet them with water, and place them immediately under a glass globe full of oxygen gas, when they will change colour; and it will be found that the change of colour is just in proportion to the quantity of oxygen each absorbs. The consequence of this absorption is the formation of an acid, in accordance with the law mentioned before. This acid changes the chlorophyllite, or green principle, from green to yellow, and then to a reddish hue. If we treat green leaves with an acid, the same changes of colour take place, and if we macerate a red leaf in potash it becomes green.

The green of leaves, and the colours of flowers, are common to all vegetables under the influence of light; but there are a number of colouring substances in vegetables which are peculiar to certain orders, and which exist as proximate elements sometimes in the leaves, in the woody part, in the juice, in the bark, in the flower, in the seeds, and in the roots. Several of these have been made subservient to our use in the art of dyeing, and will be noticed separately.

The various and beautiful colours of flowers are produced by a somewhat different process from that of the green of the leaves, in so far as they do not appear until the plant has attained a certain state of maturity. "The leaves of the plant being fully developed, they take in more nourishment from the atmosphere than what is necessary for the existence of the plant. This extra nourishment takes a new direction; a peculiar transformation takes place; new compounds are formed, which furnish constituents of the blossoms, fruit, and seed."*

Many attempts have been made to transfer the colouring matter of flowers to cloth, but without success. In general they are so fugitive as to change the moment they are brought into contact with the atmosphere, and such of them as can be extracted have no affinity for the cloth. If a third substance be used to give this affinity, it destroys the original colour of the vegetable.

It is very probable that all the colours of flowers depend

* Liebig's Agricultural Chemistry.

upon only a few proximate elements formed in the vegetable, in the manner already described, and that their various hues are the consequence of the presence of acids affecting more or less this colouring substance. This is the most probable hypothesis that has been framed, and with which we must rest satisfied till more accurate experiments verify its truth, or give us a better. The following summary of experiments will give some idea of the views held upon this subject: "The expressed juice of most red flowers is blue; hence it is probable that the colouring matter in the flower is reddened by an acid, which makes its escape when the juice is exposed to the air. The violet is well known to be coloured by a blue matter, which acids change to red; and alkalis and their carbonates first to green and then to yellow. The colouring matter of the violet exists in the petals of red clover, the red tips of the common daisy of the field, of the blue hyacinth, the hollyhock, lavender, in the inner leaves of the artichoke, and numerous other flowers. The same substance made red by an acid, colours the skin of several plums; probably, also, gives the red colour to the petals of the scarlet geranium, and of the pomegranate tree. The leaves of the red cabbage, and the rind of the long radish, are also coloured by this principle. It is remarkable that these, on being merely bruised, become blue, and give a blue infusion with water. It is probable that the reddening acid in these cases is the carbonic, which, on the rupture of the vessel which encloses it, (being a gas,) escapes into the atmosphere. If the petals of the red rose be triturated with a little water and chalk, a blue liquid is obtained. Alkalis render this blue liquid green, and acids restore its red colour."*

We need hardly mention that the influence of light in producing colours, and changing them when produced, is regulated to a great extent by the vitality of the plant; so that the effects vary in intensity according to the season of the year. When leaves or flowers are taken from a plant, they are both very soon affected by light; but it has been observed by Sir John Herschel, that flowers plucked at an early period, as when newly formed, are much more sensitive to light than at a later period of flowering, showing that flowers have a period of maturity; and if pulled at that time, the colouring com-

* Thomson's Vegetable Chemistry.

pound is much more stable, and resists the action of light much more powerfully than when pulled before they are matured. This law of development and maturity is universal, and may be the cause of many of the varieties—the superiority or inferiority of many vegetable dyes even of the same kind.

The vegetable substances used in dyeing may be divided into two classes: first, those which are used not on account of their possessing colouring properties, but because they possess matters that have a strong attraction for the fibre, which they fill, and also form insoluble compounds with the bases, and so enabling them to act the part of mordants to the substances which are afterwards to be applied; and, second, those substances that are applied or used for the colouring matter they contain.

The substances comprised in the first class of these are termed astringent, from their producing a roughening or corrugating effect upon the mouth, when tasted. All the vegetables that produce these effects are found to contain certain acids, to which this property of astringency is referable; and the presence of these acids gives them their value in the dye-house. These acids are gallic acid and tannic acid or tannin.

It has been found, from the extensive researches of Dr. Stenhouse on the vegetables containing these acids, that the tannin exists in them in a great variety of modified forms, or rather that they give certain modified reactions with chemical agents, the cause of which, analysis has not yet been able to define. For our purpose, we will divide these substances thus acted upon into two:—

1st. Those which give a black precipitate with the salts of iron—for a proper type of which may be cited galls and sumach; and,

2d. Those which give a dark-olive precipitate with iron—the type of which is catechu. The latter is much more stable in its composition, and less liable to change by standing.

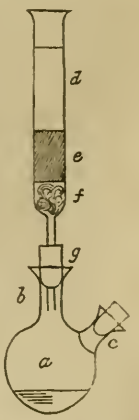
Galls.

Upon certain species of oak there grow excrescences which originate in punctures, made by a peculiar insect, for the purpose of depositing her eggs. A kind of juice exudes

from this puncture, and gradually forms round these ova hard round bodies, varying in size from one-fourth of an inch to an inch in diameter. These substances, from their resemblance to nuts, and from their bitter taste, are called gall-nuts.* By the repeated experiments of many excellent chemists upon this substance, it is considered to contain two peculiar principles. One of these, a crystallizable substance, is obtained from a macerated solution of galls, after standing in the air for a long time. This, from its possessing many acid properties, is termed gallic acid. The other is that substance which combines with skins during the process of tanning, changing them into leather, and is termed tannin, or, from its having some acid properties, tannic acid.

The best galls, according to Sir H. Davy, contain 26 per cent. tannin and 6·2 of gallic acid, but from the circumstance of these two compounds being generally found together in the same vegetable, and in variable proportions, it was thought probable that the one produced the other. This supposition was verified to a great extent by M. Pelouze, particularly as respects the tannin of galls.

The method for extracting tannin from galls is as follows:—To a vessel, such as that represented in the annexed figure, is fitted by means of a cork *g*, a funnel-shaped tube, and the neck *c* is kept corked, air-tight, during the process. At the bottom of the tube is placed a little clean cotton, as shown at *f*. Above the cotton is placed a quantity of nut-galls in fine powder, as shown at *e*. Over this is poured a quantity of common sulphuric ether, sufficient to fill the rest of the tube, as seen at *d*. A cork is then fitted tightly to the opening at the top of the tube, and the whole set aside. Next day, two layers of liquor are found in the vessel *a*, one very light and limpid, occupying the upper part, the other having a light-amber colour,



* The excrescences are produced by the *cynips* (gall-wasp) upon the tender shoots of the *quercus infectoria*, a species of oak which is common in Asia Minor. When the maggot is hatched, it eats its way out of the nidus. The best galls are those brought from Aleppo and Smyrna.

and the consistence of a syrup, occupying the lower part. These liquids are poured into a dropping tube, upon which the finger is kept, and after remaining at rest for a few minutes, they again separate; the heavy liquid is then allowed to fall out into a capsule, and the light liquid retained, so that it may be distilled for the sake of recovering the ether. The dense liquid which is in the capsule is next to be washed two or three times with sulphuric ether, and afterwards dried by a very gentle heat; the matter left has a spongy appearance, is very brilliant, and generally of a yellow tint. This is tannin in a state of purity. By this process, from 35 to 40 per cent. can be extracted from nut-galls.

M. Pelouze found that if a solution of tannin be kept closely corked from the atmosphere, no change takes place; but if left in contact with oxygen, the tannin undergoes a change, and gallic acid is formed. Hence he concludes that gallic acid does not exist except in very minute quantity in vegetables, and that the error of supposing that these two acids existed together in vegetables, arose from the method adopted to procure gallic acid, which was by allowing the macerated vegetable matter to stand in contact with the air, till the gallic acid crystallized from the solution, this being nothing more than a process for converting tannin into gallic acid by the absorption of oxygen.

This discovey is of great importance to the dyer, as it points out the evil of allowing liquids, which contain tannin, to stand exposed to the air for any length of time; for although gallic acid and tannin act in a somewhat similar manner with metallic oxides, yet the gallates are much more fugitive than the tannates. For example, if we precipitate tannic acid and gallic acid by a persulphate of iron, they are both dark blue, bordering on black; excepting a slight change of shade, the tannate remains permanent; but if the gallate be allowed to stand a few hours, it is dissolved in the supernatant liquid, and becomes almost colourless; the sulphuric acid resumes its attraction for the iron, and crystallizes as a protosulphate, (copperas,) and the gallic acid is partly decomposed and partly crystallized. These changes take place in a few minutes, if the liquor containing the precipitate be boiled.

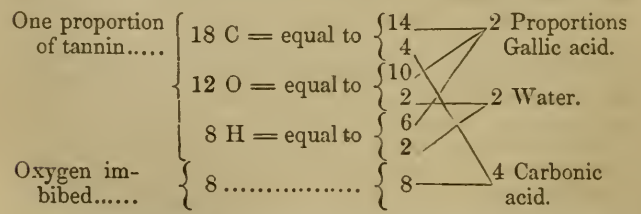
Now, if galls, or what is now more commonly used instead, sumach, be allowed to stand till after fermentation takes place, which is very soon, a great portion of the tannin is converted into gallic acid; and although the cloth dyed in sumach that is thus altered should be, as some dyers affirm, equally dark, it will not be equally fast; but from personal experience, we can say that it is neither equally dark nor equally beautiful. It cannot be so dark, for gallic acid being much more insoluble than tannin, falls to the bottom whenever it is formed, and consequently leaves the supernatant liquid much weaker in its dyeing properties.

More recent discoveries have shown that tannin is convertible into gallic acid by other and much more rapid means than being left to absorb oxygen: these are by the common processes of inducing fermentation. It is well known that fermentation is simply a derangement of the elements of certain complex compounds, and the re-arrangement of these elements in different positions and proportions, giving rise to new and altogether different compounds of a more simple nature, that is, having a smaller number of elements. The primary compounds are formed under the unknown influence of the vital principle; but whenever this is withdrawn, they seem but passively to retain their chemical conditions. The attraction of their elements seems too weak to enable them to resist any marked change of circumstances. Even a slight elevation of temperature is sufficient to overpower their affinities and induce change. As in the case of fermentation, if they are brought into contact with a body which is in the act of derangement, that body excites the same derangement in them, and the equilibrium being disturbed, the elements are left to arrange themselves according to their different attractions. If, for example, we dissolve a little sugar of grapes, which is composed of 12 carbon, 12 hydrogen, and 12 oxygen, in a little water, and raise the solution to a temperature of about 80° Fah.; and if to this we add a little yeast, which is a substance whose atoms are in the act of transposition, the yeast does not combine chemically with the sugar, but it communicates to it by contact the action of transposition, and thereby deranges the arrangement which the atoms had assumed to form sugar; and the atomic ele-

ments being thus set at liberty, begin to arrange themselves differently: every three atoms of the hydrogen combine with two of the carbon and one of the oxygen, forming four atoms of alcohol. The remaining eight atoms of oxygen unite with the remaining four of carbon in the relation of one to two, forming four atoms of carbonic acid gas. Thus the whole sugar is converted into two different substances, of which the yeast forms no part. It only acts the part of a bold revolutionizer, breaking up existing combinations, that new ones may be formed from their elements. Now tannin is found to undergo the same sort of change as the sugar, when brought into contact with certain substances; and one of the new compounds formed from this transposition is gallic acid. M. Antoine has indeed directly shown, that a very small quantity of nut-galls is capable of converting a large quantity of tannin into gallic acid, and that galls contain a substance capable of producing fermentation amongst the elements of the tannin. The composition of tannin, as compared with that of gallic acid, is as follows:—

TANNIN.	GALLIC ACID.
18 Carbon.	7 Carbon.
12 Oxygen.	5 Oxygen.
8 Hydrogen.	3 Hydrogen.

The action which is considered to take place during the fermentation of tannin by exposure to the air is, that it absorbs or combines with 8 proportions of oxygen from the atmosphere—



Now, in proportion as gallic acid is inferior to tannin in its dyeing properties, will be the extent of the evil of allowing

liquors which contain tannin, and which depend upon it for their dyeing properties, to stand till fermentation begins. In some liquors this commences in the course of three or four days; much, however, depends upon the temperature.

But although galls thus contain within them the property of a ferment, it may justly be asked whether sumach, which has in many operations of the dye-house superseded the use of galls, possesses the same property? The affirmative—that it does possess the property of exciting fermentation in other substances—has not yet been determined; but from a number of experimeuts upon the action of various substances on tannin, it would seem either to induce or facilitate fermentation; and further, we venture to say, that the tannin in sumach is more readily converted into gallic acid than the tannin of gall-nuts. If the liquor of galls be allowed to stand exposed to the air, it requires a considerable time before its tannin is converted into gallic acid, but there are a number of substances which, if put into it, cause the formation of gallic acid to proceed much more quickly. Among others, the tartaric and mallic acids possess this property in a high degree. Now, sumach, according to some recent analyses, contains a great quantity of mallic acid, which, were we allowed to reason from analogy in chemical science, places it under very favourable circumstances for fermentation. Indeed, in certain seasons of the year, we have known it to ferment in forty-eight hours. Whether this fermentation was induced first by the tannin or by the colouring matter which it contains—for sumach contains a distinct colouring matter—we cannot certainly in the meantime determine. But this we well know, that a very short exposure to the air makes it lose its colouring matter.

It was found by the author quoted above, that a little sulphuric, hydrochloric, or nitric acid, added to a solution of galls, makes it less liable to ferment by exposure.

The following table abridged from Brande's Manual of Chemistry, will give some idea of the action of some metallic salts upon a solution of galls or sumach:—

Names of Salts used.	Colour of Precipitates.
Protochloride of manganese	Dirty yellow.
Protosulphate of iron (copperas)	Purple tint.
Persulphate of iron	Black.
Chloride of zinc (muriate of zinc)	Dirty yellow.
Protochloride of tin	Straw colour.
Perchloride of tin	Fawn colour.
Sulphate of copper (blue-stone)	Yellow brown.
Nitrate of copper	Grass green.
Nitrate of lead	Dingy yellow.
Tartrate of antimony and potash	Straw colour.
Tartrate of bismuth and potash	Copious yellow or orange.
Sulphate of uranium	Blue black.
Sulphate of nickel	Green.
Protonitrate of mercury	Yellow.

In attempting to draw a practical inference from some of these results, we would, for example, conclude that persulphate of iron is much better adapted for dyeing blacks than protosulphate, as the former is mentioned as producing a deep black, while the latter gives only a purple tint. It is much to be regretted that in making out these tables, care is not taken to give the results in all their bearings. What is mentioned of these two salts is correct, at the instant the mixtures are made; but in the course of twenty minutes the black from the persulphate becomes a brownish slate, whereas the purple tint of the protosulphate changes during the same time to a deep black; and these changes continue till the former has become a light yellowish slate, and the latter a perfect ink black.

When trying the difference of effect produced by the persulphate and protosulphate of iron upon pure tannin and gallic acid, it may further be observed, that the changes produced with tannin are somewhat similar to those which occur in a solution of galls. With gallic acid the persulphate gives at first a black precipitate, not so dark as the tannate, but in a few minutes it changes to an olive, and continues changing till it becomes almost colourless. With the protosulphate, at first the colour is scarcely visible, but after an hour's exposure, it assumes a rich violet. From these facts, it may be concluded, that tannin is superior to gallic acid as a dyeing

agent for black; moreover, the compound formed is more insoluble.

Another circumstance which modifies the results of these experiments in their application to dyeing, is the quality of the water used. If the experiments be performed with distilled water, it will be found on repeating them with common spring water, that one-half of the quantity of stuffs will give the same depth of colour; and that the colours, in this instance, have more of a purple hue, and are much more permanent. This may be illustrated by a very simple experiment. Take two glass jars of equal size, fill them half full with distilled water, and add an equal quantity of a solution of galls, or sumach; put into each an equal number of drops of a solution of protosulphate of iron (copperas); the change of colour is scarcely perceptible. But fill up one to the brim with spring water, and it almost instantly becomes a dark reddish black. Allow both jars to stand for an hour, the solution with the distilled water will have become a deep violet, while the other, nowithstanding the double quantity of water, is so dark that no light is transmitted; and it will require one-half more water to reduce it to the same shade as the other, but still retaining more of the reddish hue—which, by the way, makes it superior for black. It will also be found to be much more insoluble, and to require a greater proportion of acid to decompose it. If soft or filtered river water be used instead of distilled water, the distinction is not so great, but still, the difference is equal to one-half. The best water which we have experienced for dyeing black, and other *saddened colours*,* gave by analysis, sulphuric, muriatic, and carbonic acids, lime, a trace of silica, and iron. The whole solid contents did not exceed one grain in a fluid ounce, or 160 grains per gallon, which, we may remark, is a large quantity, (see page 40.) These ingredients probably existed in the water as sulphate, carbonate, and muriate of lime, and carbonate of iron. The iron was in very small proportion; the carbonic acid and lime greatest.

Now a dyer, learning his trade in a work where such water was used, could not fail to become a successful dyer of all saddened colours; but were he taken from this work to

* A technical name for colours that are darkened by sulphate of iron, which includes drabs, fawns, slates, gray, some kinds of browns, blacks, &c.

another where soft filtered water was used, what would be the result? When he attempted to dye a black with the same quantity of dyestuff he formerly used, he would only produce a dark-slate colour; and if he wished to obtain a slate colour, he would produce a gray. In this dilemma, the dyer adds stuff till he comes to the desired shade; but fancy-dyes, bolstered up with stuffs, are not so pretty; besides, the employer, in consequence of this extra stuff, must either submit to a loss, or discharge the dyer; who, no doubt, considering himself ill-used, talks loudly of his ability in dyeing such colours, and offers to prove that the fault is not in him but the water. Were this wholly a supposed case, we would pause here, and make an apology to our brethren for these remarks; but not being so, we will rather endeavour to show that the fault is the dyer's. Dyeing being an art wholly dependent upon chemistry for its development and successful practice, he who practises it, without studying chemistry, is like a boy learning to repeat a number of choice sentences from an author, without knowing his letters. Had the dyer, alluded to, known the principles of chemistry, so far as they are applicable to his trade, he would, on finding that the same quantity of stuffs did not yield the same results, have examined the water to discover where lay the difference, and in this particular case he would find, that instead of adding an extra quantity of sumach, copperas, and logwood, to get a good black, a little chalk and hydrous gypsum (sulphate of lime) added to the water, would so qualify it as to render it equally effective with that to which he had been accustomed.

There are several kinds of galls, but the following three kinds occur in commerce—Aleppo galls, Smyrna galls, and East Indian galls. These three kinds consist, according to the ripeness of the apples, of black, green, and white galls. When the galls occur in commerce mixed, they are termed "natural;" and are sorted into the following kinds:—picked black, natural black, (consisting of black and dark-green galls), dark green, light green, natural white (light green and white galls), and picked white. Aleppo galls are the best; but under this name must be reckoned not only such as come from Aleppo, but also those derived from Mosul in Natalia, and which are therefore called in Constantinople and Smyrna lists, not Aleppo, but Mosul galls. This gall recom-

mends itself by its heaviness, and the lighter-coloured kinds (white and light-green galls) are frequently remarkable from their large size; but the best distinguishing character between the Mosul and Smyrna galls, is the darker kind of the Mosul galls having as it were a blueish bloom, while the Smyrna are of a grayish colour. The Mosul gall, moreover, has not so many tubercules as the Smyrna kind. The first is exported from Constantinople and Smyrna, the latter principally from Smyrna. The chief markets are Trieste, Leghorn, Marseilles, and London. The fourth kind of nut-gall is the marmorated one, which is brought from Puglia; the chief staple places are Naples and Trieste. It consists generally of large apples, which have fewer tubercules, and these not acute. They are generally of a whitish-red and greenish colour, sometimes also darker. Istria produces a very inferior kind of galls; they are small, commonly of a reddish colour, and are much tuberculated. Place of export, Trieste. These are the principal kinds, not to mention others of rare occurrence; for instance, a kind of gall is brought from Asia Minor and Dalmatia, which is hollow, not heavy, and of a reddish colour.

Analysis of galls by M. Guibourt:—

Woody fibre	10·5	The *luteo gallic* acid is applied to the yellow colouring matter of the galls.
Water	11·5	
Tannin	65·0	
Gallic acid	2·0	
Ellagin acid and luteo gallic acid	2·0	Sometimes white galls are dyed by a little iron water being put upon them, which darkens them, and makes them appear of a better quality.
Extractive matter	2·5	
Gum	2·5	
Starch	2·	
Clorophylle	0·7	
Sugar	1·3	
	100·0	

Sumach.

Called by botanists *rhus coriaria*, is a native of Syria. It is diligently cultivated in Spain, Portugal, and in some parts of Italy and Sicily, and known in the market as Sicily, Malaga, Trieste, and Verona: the first is the best quality. A quantity of about 60,000 tons of this dye is used annually in this country. The sumach tree, or rather shrub, grows to a height of about eight or ten feet; the stems are ligneous, and divide at the bottom into many irregular branches; the bark is hairy and of a brown colour. The leaves are winged, have seven or eight pair of jagged lobes, and terminate in an odd one. The leaves are placed alternately upon the branches, which are surmounted by flowers of a greenish-white colour. The shoots of the shrub are cut down every year close to the roots, and after being dried, are reduced to powder by means of a mill; the very fine stems are often cut into small pieces, and put amongst the powder.

We have already referred to the use of sumach in the dye-house; we speak of it simply as a fit substitute for galls, possessing similar properties, and seemingly passing through similar decompositions by exposure. A little sulphuric acid added to sumach retards fermentation, but it is not a good addition when dark shades are required, and should only be used for sumach which is to stand for some time, or which is to be used for very light drabs. In this case the colour obtained is more pleasant—technically more *sweet;* but either the addition of acid, or by standing exposed to the air, very soon destroys the colouring matter which sumach contains, and also the depth of shade of dye obtained from it. It is, therefore, always advisable to use the sumach newly boiled. The comparative advantages of using it newly boiled and after it has been kept for some time, can easily be ascertained by taking a given quantity, boiling it, and allowing it to stand over a few days; then taking the same quantity, boiling it the same length of time, heating the old solution to the same temperature as the new, and adding to each the same weight of cotton; the effects produced will be very different, and will, more than any written description, show the importance of attending to this circumstance.

Sumach is generally used when the metallic base, or mordant, is iron or tin, and is therefore the *bottom* * of blacks, reds, &c. Sicilian sumach has a greenish-yellow colour. When bright colours of red are to be dyed it is best; also for barwood, and all colours that require clearness. Verona sumach when compared with Sicily has a fawn tint; it is best for deep reds, browns, and blacks. When used for barwood reds the colour is heavy, and to use Sicilian sumach for the purposes that Veronian is most suitable, would require about one-half more in quantity for the same weight of cloth.

The following process for dyeing black will enable us to illustrate some of the reactions of this substance in connection with the metallic bases:—

The goods are allowed to steep in a decoction of sumach for twelve hours; they are then wrought through lime-water, which gives them a beautiful blueish-green colour, becoming very dark with a short exposure to the air. If allowed to stand for half-an-hour, the green colour passes off, and the goods assume a greenish-dun shade. When they are at the darkest shade of green, they are put through a solution of copperas; after working some time in this, and allowing them to stand exposed to the air, they become a black. But if dried from this, it is only a slate or dark gray. They are therefore again put through lime-water, which renders them brown, and then wrought through a decoction of logwood till the colour of the wood has nearly disappeared. A little copperas is added, which throws off the reddish hue of the wood, giving them a blue shade. This is termed *raising* the colour. The goods are washed from this in cold water, and dried in the shade. When a deep blue-black is wanted, the goods are dyed blue previous to steeping in the sumach.

The passing of the goods from the sumach through lime, before introducing them into the iron solution, is not essentially necessary for producing the colour, but is very useful in facilitating the operation, and in giving depth of hue by the iron. This metal is held by the strong affinity of the acid, but the goods, impregnated with lime, being put into the copperas, the lime takes the acid, and the iron, liberated immediately and in greater quantity, takes to the tannin of the

* Bottom is a technical term applied to the preparation of cotton by sumach and the like, for colours.

sumach. The passing through lime-water from the copperas solution, is for the purpose, also, of neutralising the acid of the iron upon the goods, which, as a salt, would act upon the logwood, and injure the operation. Washing out of the copperas answers equally well, and for fine goods, where a soft tint of black is necessary, is even preferable. When the goods are passed through the lime, the presence of the alkali is hurtful to the logwood; therefore it is best to pass the goods through water before entering them into the logwood. The action of the iron upon this substance is the same as we have described for galls; a persalt of iron added or used, gives an immediate black, but not permanent; the oxygen seeming to affect the decomposition of the colour in some way. When a protosalt of iron, as copperas, is used, the blackening is slower, but more permanent; showing that it is the most suitable salt to use. It is, however, to be remarked, that the combination of iron and tannin, forming the black colour, seems to depend on a state of oxidation of the iron a little higher than the protoxide, and much lower than the peroxide; that the peroxide when used, is reduced in oxidation, and causes change and loss in reduction, and that the protoxide imbibes oxygen as required.* Upon this important inquiry we quote the following from an article by M. Barreswil in the *Chemical Gazette*, translated from the *Comptes Rendus*:—

"When a solution of gallic or of tannic acid, which are colourless, and generally form colourless salts or of the colour of the bases, is poured into a solution of the persulphate of iron, an intense blue precipitate is formed, which remains suspended in the liquid. This anomalous fact has frequently excited the attention of chemists, MM. Berzelius and Chevreul have even expressed some doubts respecting the simplicity of the reaction.

"It has long been known that tannin and gallic acid do not precipitate the protosalts of iron when protected from contact with the atmosphere. Berzelius, Chevreul, and Persoz, have, moreover, observed that when gallic acid or tannin is conveyed into a salt of the peroxide of iron, it is always reduced to the state of a protosalt. This fact is easily proved

* An opinion urged several years ago by the author in the *Practical Mechanics' and Engineers' Magazine.*

by adding to the blue solution produced by the persulphate of iron in a solution of gallic acid, an excess of acetate of lead or of carbonate of lime, which precipitates the blue combination, and at the same time the sulphuric acid. A colourless liquid is separated by filtration, in which the presence of iron may be demonstrated in the state of protoxide.

"These experiments are insufficient to explain this curious reaction. It is not improbable to admit, as MM. Berzelius and Chevreul have done *à priori*, that the oxygen combining with the gallic acid or the tannin converts them into a new acid of a blue colour; but positive experiments were wanting to decide the point.

"When a solution of tannin or of gallic acid is poured by drops into a solution of persulphate of iron in excess, no blue colouring is obtained; if there is one produced it is only momentary. Nor is there one formed with the same salt in minimum in presence of chlorine, nor with a protosalt of iron and gallic acid oxidized in various degrees by chlorine, by a salt of silver, or lastly, by the atmosphere in an alkaline solution.

"When a solution of gallic acid in excess is conveyed into persulphate of iron, and the liquid thrown down by acetate of lead, a blue paste is obtained, which treated with oxalic acid forms soluble oxalate of iron; the blue colour disappears entirely, and is restored by acetate of soda. The solution of the oxalate, diluted very much with water, treated cautiously with the two prussiates and sulphuretted hydrogen, presents all the characters of the salts of iron in the state of peroxide and protoxide.

"It appears to me that we may conclude from the above facts, that if we start with a protosalt of iron, it is requisite to add oxygen, and if we set out with a persalt, some oxygen must be removed, in order to produce the blue compound, and that this compound contains the two oxides. In the first case the protoxide of iron combines with the oxygen of the atmosphere; in the second, a portion of the oxygen of the peroxide destroys a corresponding portion of the gallic acid or of the tannin, converting it into a brown substance. This substance does not enter into the constitution of the new compound, which must be considered as a salt formed of tannin or gallic acid and of an intermediate oxide of iron, probably of a blue

colour, the tint of which is slightly altered by this brown substance.

"To prove in the most evident manner that the blue colouring is not to be ascribed to a blue acid, but to a particular oxide, I endeavoured to obtain other blue salts with mineral acids, for instance with sulphuric acid. For this purpose I prepared some mixtures in variable proportions of the protosulphate of iron and of the persulphate, and to avoid an inevitable separation of the two salts from their different degrees of solubility, I removed *immediately* the water by adding to the solution concentrated sulphuric acid in large excess, taking care to produce as little heat as possible. In this manner I obtained a thick paste of a *deep blue*, the tint of which was more or less pure according to the proportions of the two salts of iron; I likewise produced a blue sulphate, but of very ephemerous existence, by evaporating rapidly a mixture of the two salts of iron; the blue tint appeared at the moment when the mass was nearly dry. On substituting phosphate of soda for the sulphuric acid, I obtained a deep-blue phosphate of iron and some sulphate of soda, which removed the water immediately. I endeavoured, but without success, to prepare combinations with other salts; the hyposulphite of soda alone afforded an intense blue colouring, but of remarkable instability. This is not surprising; there are many instances in chemistry of bases which prefer combining with certain acids and refuse to unite with others; such for instance, among others, is the protoxide of copper.

"I made numerous experiments to obtain the blue oxide in a free state; I succeeded several times, but under circumstances which I was not able to produce at will. It is, however, a well-known fact, that when a protosalt of iron is precipitated with ammonia in contact with the atmosphere, the white precipitate of the protoxide soon becomes green, passing first, however, through blue.

"The impossibility of obtaining the blue sulphate of iron in a crystalline state, and of isolating the acid of the blue gallate compound, prevented me from having recourse to analysis in order to arrive at the formula for these intermediate salts: I was forced to proceed by synthesis, which I confess is far from being accurate; and it is with some doubts that I publish the results.

"Of all the mixtures of protosulphate and persulphate which I experimented on, that which afforded the most pure blue with sulphuric and gallic acids and with the phosphate of soda, contained precisely 3 equivalents of protosalt to 2 of the persalt—proportions which correspond to the cyanide $Fe_7 O_9$, prussian blue.

"If, as I hope, I have rendered probable the existence of two intermediate oxides of iron, capable of forming salts and of entering into the salts with their peculiar colour, I shall have thrown some light on the various tints produced by the different kinds of astringent substances, morphine, salicylic acid, and some other organic principles; and likewise on the production of violet, black, brown, and green tints, with red and yellow-colouring principles, in presence of salts of peroxide of iron. I have convinced myself that all the yellow-colouring substances (for instance curcuma) do not produce green; that the red-colouring principles (among others aloetic acid) do not give a violet; and that when there is a production of green, (as with the Persian berries and the Quercitron,) or of violet, (as with madder, logwood, &c.,) the phenomena are identical with those which occur with tannin and gallic acid. These observations agree, moreover, perfectly with the suppositions of M. Thenard, with the facts published by M. Köchlin-Schouch, and by M. Schlumberger, and which M. Stackler informs me he has found confirmed in his establishment, that the iron mordants should be at a fixed degree of oxidation to produce beautiful dyes."—*Comptes Rendus.*

CATECHU.

This is another substance containing much tannin. We have already noticed some of its peculiarities, but may state further that it is a dry extract prepared from the wood of a species of sensitive plant, named *acacia catechu.* It was long considered an earthy substance, and termed *terra Japanica.* The plant is indigenous to Hindostan, and flourishes abundantly in mountainous districts. It grows to about twelve feet in height; the trunk is about a foot in diameter, and covered with a thick dark-brown bark. The extract which is obtained from the tree is made from a decoction of

the wood. As soon as the trees are felled, all the exterior white wood is carefully cut away, the interior, or coloured wood, is then cut into chips; narrow-mouthed unglazed pots are nearly filled with these, and water is added to cover them. Heat is applied, and when half the water is evaporated, the decoction, without straining, is poured into a shallow earthen vessel, and further reduced two-thirds by boiling. It is then set in a cool place for a day, and is afterwards evaporated by the heat of the sun, care being taken to stir it occasionally during that process. When it is reduced to considerable thickness it is spread upon a mat or cloth, which has been previously covered with the ashes of cow dung, and this mass divided by a string into quadrangular pieces, is completely dried in the sun, and is then fit for sale.

It is a brittle compact substance, of a dark-brown or chocolate colour; has no smell, but a very stringent taste; is soluble in water; contains a great amount of tannin, and a peculiar acid, which has been named catechuic acid. It is the reactions of these ingredients with oxygen and other chemical agents, that constitute its dyeing properties. A solution of catechu in water is a beautiful reddish-brown colour, which ought to be kept in mind in perusing the following summary of the reactions of other substances upon it:—

Acids brighten the colour of the solution; alkalis darken it, and the shade deepens by standing; protosalts of iron give olive-brown precipitates; persalts of iron also give olive-brown precipitates, but with more green than those of the protosalts; salts of tin give yellow-brownish precipitates; nitrate and sulphate of copper, yellowish-brown; acetate of copper, a brown precipitate; salts of lead, brick-coloured precipitates; bichromate of potash, a deep red-brown. These reactions alone indicate how very important an agent catechu may be in the hands of the dyer, and how very extensive its applications in the processes of his art.

There are various qualities of catechu in the market, differing considerably in their value as a dye. The Bombay catechu is met with in square masses, of a reddish-brown colour, and which, when broke, exhibit a uniform texture. Its composition is as follows:—

Tannin	52
Gum	7
Extractive matter	34
Impurities	7
	100

"Extractive matter" is a sort of indefinite term, applied to designate a brown matter extracted from vegetables when boiled; its true nature is not known, but the part it may play in the reactions of catechu is probably important, and is at least not to be overlooked.

Bengal catechu is met with in flattish round lumps, of a light-brown colour outside, but dark internally. It gives:—

Tannin	49·5
Gum	7·0
Extractive matter	36·5
Impurities	7·0
	100·0

Malabar catechu is imported in large masses, of a light-brown colour outside, dark within, and covered with leaves. It gives:—

Tannin	45·8
Gum	8·0
Extractive matter	39·9
Impurities	6·3
	100·0

There is a sort of catechu brought to this country from India in small cubical masses, about an inch in size. This is a very inferior quality, and, as imported, is easily known from genuine catechu. Sometimes, however, means are resorted to, to alter the colour of this spurious article, and make it more difficult to be detected. It is said often to contain a great quantity of roasted starch, or British gum, termed dextrine.

Catechu is often adulterated by other vegetable extracts, and also by sand, clay, and ochre. These last impurities may be readily detected by dissolving a portion of the catechu in

water, when any of them contained in it will be precipitated; or by burning a little of it in a crucible until all organic matter is consumed, when the latter adulterants will remain. We have examined samples of catechu of good colour, having $8\frac{1}{2}$ per cent. of clay and sand mixed with them. Good catechu is all soluble in cold water, and gives a clear solution.

The tannin which is in catechu is not converted into gallic acid by exposure so easily as that in galls; but it is subject to oxidation. When a portion is dissolved in water, the solution has a gummy character, and goods put into it would be affected as by a weak solution of gum; the threads of yarn, for example, adhere when dried out of it. The addition of a metallic salt destroys this viscous quality, and those salts answer best, or are most effectual for that purpose, which yield their oxygen most easily. Accordingly, the salts of copper are most commonly used, and they are added to the dissolved catechu before putting in the cotton. The chemical changes which catechu undergoes in the operations of dyeing, are not yet well understood. The action has been explained in this way:—The copper salt oxidizes a portion of the catechu, which, although insoluble in water, is soluble in deoxidized catechu; therefore, the whole is held in solution in the bath; the goods become impregnated with this solution, and as the whole of the catechu upon the cloth becomes oxidized, it becomes also dark. This explanation does not account for all the phenomena occurring during the dyeing of browns, &c., with this substance; for if we take two portions of a solution of catechu, and to the one add a salt of copper, to the other a salt of zinc, pass the cloth from these through a solution of lime, and expose to the air, the piece treated with the zinc will become dark brown, but not that treated with the copper. The above explanation would lead us to expect the opposite, as copper yields its oxygen more easily than zinc. When catechu is oxidized, there is formed an acid nearly of the composition of gallic acid, which has a deep-brown colour. This is formed when catechu in solution is treated with alkaline matters. The lime, therefore, in the above experiment, may have acted the principal part; but cotton from catechu solution, put through acetate of lead, also gives a deep-brown colour without alkali. When

goods impregnated with catechu are passed through bichromate of potash, there is obtained a deep brown: an oxidation of the catechu takes place at the expense of the chromic acid. Whether the oxide of chromium may act as a base on any part of the dye, we cannot positively affirm; but on burning cotton dyed brown by this means, there is obtained in the ash the oxides both of chrome and of copper; showing that both the copper and chrome used, play a part in forming the dye: and that the dye by this method is something more than mere oxidation of the catechu, as in passing the cloth from the catechu through bleaching liquor.

The reactions of catechu are so varied, that it is now used for almost all compound colours, blacks, browns, greens, drabs, and fawns; and its permanency renders it of high estimation in the market.

The following is the analysis of a sample of catechu by Mr. Cooper, giving a wider range to the matters contained in it, and which will serve to give some better idea of the varieties of this substance; for, from its mode of preparation, probably no two samples will give the same proportions:—

Tannin	62·8
Extractive, or colouring matter	8·2
Resinous matter	2·0
Gummy matter	8·5
Insolulable matter	4·4
Water	12·3
	98·2

Valonia Nuts.—These are the cups of the acorn from the valonia oak, which grows in the Dardanelles and the islands of the Archipelago, and throughout all the maritime ports of Asia Minor. They are imported in great quantities from Smyrna and its neighbourhood. These contain a great quantity of tannin, and also gallic acid; but they are inferior to sumach or galls for dyeing cotton, and for giving depth of colour with the salts of iron. For silk, however, they possess some peculiarities exceedingly valuable for blacks, giving a permanency not obtained with the ordinary galls; and moreover, the production of the proper black with valonia nuts upon silk requires a certain treatment which few dyers have attained,

particularly in Scotland. We cannot, for instance, furnish a black upon silk which will withstand unchanged all the operations which a hat undergoes in the process of manufacture—a purpose for which we understand the valonia black is applied.

Divi Divi—Or *Libi Davi*, is the pod of a leguminous shrub, a native of South America; it has been tried as a dye instead of galls or sumach, but is not much used now, if at all.

Myrobalans.—This is the fruit of a tree which grows in India; it is imported into this country in various forms, has a pale-yellow colour when new, but becomes darker by age, and then resembles dried plums. It contains tannin, and is sometimes used on that account for the operations of dyeing. Its reactions with iron, tin, and alum, are similar to those of sumach, but of less value.

Oak bark contains a great quantity of tannin, and is used on that account for tanning skins, but it is not much employed in the dye-house, although it may be used for similar purposes as sumach. The bark of the mangrove tree also contains tannin in considerable quantity; there are, indeed, very few vegetables which have not in their composition more or less of tannin, and which may not be used in virtue of this property instead of galls or sumach; but the quantity in them being much less than in sumach, they are not cultivated for that purpose. The bark of the ash, willow, hazel, birch, broom, &c., are often used for dyeing woollens by country people; and some of these substances possess peculiar dyeing properties. The husks of several nuts also contain much tannin. The walnut, for instance, has been long used and much esteemed by the French dyers for woollen stuffs; it gives very fast shades, without previous mordanting, although alum is sometimes used to give variety. The outer peel of this nut is collected for the dyers; they are put into large casks, with water poured over them, and kept for a year or more, as they improve while this process of maceration is prolonged. The roots of the walnut tree are also used for dyeing browns. The husks of the horse-chesnut likewise possess dyeing qualities, and might be applied advantageously for some purposes. Mahogany saw-dust, although not affected much by mordants, possesses dyeing properties of considerable value, yielding with iron a variety of shades of great permanence and beauty.

Many of the dye-woods which are used for their colouring matter contain tannin, the action of which upon the mordants is often very injurious to the tint. Many varieties of the different woods, giving the same colour, depend much upon the presence of tannin. The whole woody matter being boiled to extract the colouring matter, the tannin is also dissolved, and it is sure to act upon the mordant in the process of dyeing, producing an effect very similiar to that of adding a little sumach to the colouring matter. In many cases this is done beneficially, but in other cases it would deteriorate the tint required. In such cases the presence of tannin in the colouring matter obtained from the wood does not suit. Mr. Warrington proposed as a practical means of ascertaining the quantity of tannin in any matter, the following test:—Premising that a solution of gelatine, isinglass, or glue, precipitates tannin: making a given quantity of this solution by adding drop by drop to a given quantity of the substance to be tested for tannin, also in solution, as long as a precipitate is formed, and marking in the alkalimeter the quantity of gelatine used; every three grains of pure gelatine is equal to two grains tannin, and accordingly it is easy to arrive at a near approximation of the quality of these dyestuffs. This operation will, no doubt, require a little experience, but it is easily performed, and well deserves attention.

INDIGO.

In the few introductory remarks we made upon vegetable colours, we mentioned that, besides the green of leaves and the colours of flowers, which we considered common to all vegetables, there were other colouring matters, which existed only in certain kinds of vegetables, and in particular parts of the vegetable. Indigo is one of these: it belongs to a genus of leguminous plants found in India, Africa, and America, named *indigofera*. Botanists have described about sixty species of this genus. These all yield indigo; but the species from which it is usually extracted are the *I. anil.*, the *I. argentea*, and the *I. tinctoria*. It is also extracted from a tree very common in Hindostan, (the *nerium tinctorium* of botanists,) and from the woad plant, (*isatis tinctoria*,) which is a native of Great Britain, and of other parts of Europe. The colouring matter of these plants is wholly in the cellular tissue of the leaves, as a secretion, or juice—not, however, in the blue state in which we are accustomed to see indigo, but as a white substance, which as we shall presently see, remains white, so long as the tissue of the leaf remains perfect. When this tissue is by any means destroyed, the indigo absorbs oxygen from the atmosphere, and becomes blue.

Of the early history of indigo little is known; neither is it known when it was first used as a dyestuff. The Greeks and Romans used it as a paint, under the name of *indicum*. Its value as a dyestuff was not known in Europe till nearly the close of the sixteenth century, when it was imported from India by the Dutch; but our legislators, for a long time, prohibited its use in England under severe penalties. These prohibitions continued in force till the reign of Charles II., and the reason assigned was, that it is a corrosive substance, destructive of the fibres of the cloth, and therefore calculated to injure the character of the dyers of this country. This opinion, no doubt, sprung from the strong and interested opposi-

tion to its use by the cultivators of the woad, which was then regarded as an important branch of national industry.

"When indigo was first introduced, only a small quantity was added to the woad, by which the latter was much improved; more was afterwards gradually used, and, at last, the quantity became so large, that the small admixture of woad served only to revive the fermentation of the indigo. Germany thus lost a production by which farmers, merchants, carriers, and others, acquired great riches. In consequence of the sales of woad being so much injured, a prohibition was issued against the use of indigo in Saxony, in the year 1650; and in the year 1652, Duke Ernest the Pious caused a proposal to be made to the diet by his envoy, that indigo should be entirely banished from the empire, and that an exclusive privilege should be granted to those who dyed with woad. This was followed by an imperial prohibition of indigo on the 21st of April, 1654, which was enforced with the greatest severity in his dominions. The same was done in France; but in the well-known edict of 1669, in which Colbert separated the fine from the common dyers, it was stated, that indigo should be used without woad, and in 1737, dyers were left at liberty to use indigo alone, or to employ a mixture of indigo and woad."—*Barlow's Manufactures and Machinery of Great Britain.*

The plant which yields the indigo in Bengal is a small straight plant, furnished with thin branches, which spread out and form a sort of tuft; the average height is four feet, but on good ground it sometimes attains a height of even seven feet. The leaves are soft, and somewhat like those of the common clover, and the blossoms are of a light-reddish colour. The plant is at its greatest perfection, and yields the greatest quantity of indigo, when in full blossom.

There are two methods of extracting the colouring matter from the leaves: the first is by fermentation and beating. This process is conducted in two large brick cisterns or vats, built in relation to one another, like two steps of a stair. The upper one is termed the steeper, because in it the fermentation is conducted. At the bottom of this cistern there is a plug-hole through which, when the process of fermentation is finished, the fluid is run off into the lower cistern, denominated the beater, because in it the process of beating the fluid

by paddles, to separate the feculæ from the water, is performed. The plant, when cut, is tied up in bundles about five feet in circumference, and conveyed as quickly as possible to the vat; for, were it kept but a short time in heaps, the indigo in the plant would be destroyed. The upper vat is filled to about five or six inches from the top with these bundles laid in regular tiers. To prevent the throwing up of the herb by the swelling and agitation caused by the fermentation, there are irons built in the two side walls, opposite to one another, to which are fastened beams of wood, which traverse the whole length and breadth of the vats. When the vat is sufficiently filled with the vegetable, a strong grating of bamboo, large enough to cover the whole surface, is laid over the plant, and fastened down by the cross beams. These precautions being completed, cold water is poured as quickly as possible into the vat, till the surface rises within three or four inches of the upper edges. In a short time fermentation commences, and is completed in from nine to twelve hours. Towards the end, the action is very brisk, swelling and throwing up frothy bubbles, which sometimes rise like pyramids. These bubbles are white at first, but after a little exposure to the air, they become blue, and then purple. This part of the operation requires great skill. If the fermentation be too long, the indigo will be much damaged; and, if too short, the quantity is much diminished. When the liquor ceases to swell, it is let out into the second or beating vat, and is then of a light-green colour.

The liquor being now in the lower or beating vat, a number of men enter it, furnished with oar-shaped paddles, about four feet in length; they continue to walk backwards and forwards, agitating or beating the liquor with these paddles. At the commencement of this agitation, the liquor begins to froth; but this is prevented, provided the fermentation has not gone on too long, by a few drops of oil. In the course of an hour and a-half, the liquor begins to granulate, and assume the appearance of agitated water, full of wood grounds or sawdust. This part of the process also requires considerable care and management; for, if the beating be stopped too soon, the indigo will not be all separated from the liquor, occasioning a proportionate loss; if continued too long, the granulated particles are broken, and disposed through the

liquor, and do not readily fall to the bottom. When the beating is completed, the vat is allowed to settle; the grains which constitute the indigo fall to the bottom, and the supernatant liquor is let off by plug-holes in the side of the vat. The precipitate is then removed to a copper boiler, to which there is a fire kept till the liquor becomes as thick as oil. Some manufacturers bring it to this state by causing the liquor to boil; others by keeping it at a moderate temperature. The former process produces lighter indigo than the latter. In this state it is put into a large flat vessel, furnished at the one end with a cloth filter. After most of the liquor has filtered through, the indigo remains in the vessel about the consistence of butter. It is then put on proper frames, and subjected to considerable pressure by a sort of screw-press; and is now ready to be cut into small cakes, which are placed upon boards in a drying stove; when dry, these cakes are packed up, and in this state form the indigo of commerce.

The other method of extracting the indigo from the plant differs from that described, only in the first operations. Instead of putting the plant into the vat when newly cut, it is spread out, to dry in the sun for two days, and then thrashed to separate the leaves from the stems. The leaves are then kept until they have changed from a green to a blueish-gray, or lavender colour; they are then put into the first vat with warm water, and kept stirring till the leaves are so completely wetted as to sink. The liquor is then instantly let off into the beating vat, where it is treated as already described.

The chemical changes which take place during these operations are not well understood, and the various opinions expressed by chemists concerning them are not very easily reconciled. Berthollet in his Elements of Dyeing, while describing the process of the first or fermenting vat, says, "In the first a fermentation is excited, in which the action of the atmospheric air does not intervene, since an inflammable gas is evolved. There probably results from it some change in the composition of the colouring particles themselves, but especially the separation or destruction of a yellowish substance, which gave to the indigo a greenish tint, and rendered it susceptible of suffering the chemical action of other substances. This species of fermentation passes into a destructive putre-

faction, because the indigo, as we shall see, has a composition analogous to that of animal substances."

Dr. Ure, in his Dictionary of the Arts and Manufactures, says, that from some experiments made upon the gases given off during fermentation, they were found to be composed, when taken about the middle of the operation, of 27·5 of carbonic acid gas, 5·8 of oxygen, and 66·7 of nitrogen, in the 100 parts; and towards the end of the operation, they consisted of 40·5 of carbonic acid gas, 4·5 of oxygen, and 55 of nitrogen. No carburetted hydrogen is disengaged. "The fermenting leaves," using the Doctor's words, "apparently convert the oxygen of the air into carbonic acid, and leave its nitrogen free." They also evolve a quantity of carbonic acid spontaneously. It will be observed that these two opinions are decidedly contradictory; the one says that the action of the atmosphere does not intervene, and that an inflammable gas is evolved; the other, that there is no inflammable gas evolved, and that the air is apparently the principal agent in effecting the various changes. But when we recollect that the leaves are all under the liquor, and kept so by the fixed position of the beams, there can be little contact between the fermenting leaves and the air, except that held by the water, and among the leaves, and of the plants themselves; hence the conversion of its oxygen into carbonic acid gas must be very limited.

Sir Robert Kane says of this process:—"After some time a kind of mucous fermentation sets in; carbonic acid, ammonia, and hydrogen gases are evolved, and a yellow liquor is obtained, which holds the indigo dissolved. The theory of this action is, that by the putrefaction of the vegeto-animal matter of the leaves, the indigo is kept in the same white soluble condition in which it exists in the plant."

Dr. Thomson, in his Vegetable Chemistry, supposes that the indigo exists in the plant in union with another substance, and during fermentation that substance is decomposed, and carbonic acid gas consequently evolved. But we will give his own words:—"The leaves of the indigofera yield a green infusion to hot water, and a green powder may be precipitated from it; but unless a fermentation has taken place, neither the colour nor the properties have any resemblance to those of indigo. There is little doubt that in the leaves it exists in

the state of *white* or *deoxygenated indigo*, and that during the fermentation, it combines with the requisite quantity of oxygen to convert it into *blue indigo*. The evolution of carbonic acid gas renders it not unlikely that the *white indigo* was in combination with some principle (probably of an alkaline nature) which was decomposed during the fermentation."

These discrepancies of opinion relative to the nature of the changes which take place during fermentation, show that proper investigations have not yet been made into this part of the process: and it is obvious that until this be done, any hypothesis founded upon statements concerning the gases evolved, must be unsatisfactory. The supposition hazarded by Dr. Thomson certainly appears to us the most consistent; for as deoxidized indigo combines readily with alkaline substances, and as the vegetable alkalis almost always contain nitrogen, we can easily conceive of that gas being evolved either free or in combination with hydrogen, forming ammonia. It may yet be found that indigo, like gallic acid, does not exist in the living vegetable, but is the result of a decomposition of some more complicated compound.

The chemical action which takes place in the second vat in which the beating process is conducted, is apparently much more easily explained, and therefore the discrepancies among writers on the subject are not so great. We shall give only two quotations. Berthollet says, "Hitherto the colouring particles have preserved their liquidity. In the second operation the action of the air is brought into play, which, by combining with the colouring particles, deprives them of their solubility, and gives them the blue colour. The beating serves at the same time to dissipate the carbonic acid formed in the first operation, which action is an obstacle to the combination of the oxygen." Dr. Ure's opinion is thus expressed: —"The object of the beating is threefold; first, it tends to disengage a great quantity of carbonic acid present in the fermented liquor; secondly, to give the newly-developed indigo its requisite dose of oxygen by the most extensive exposure of its particles to the atmosphere; and, thirdly, to agglomerate the indigo in distinct flocks or granulations. In order to hasten the precipitation, lime water is occasionally added to

the fermented liquor in the progress of beating; but it is not indispensable, and has been supposed to be capable of deteriorating the indigo."

That the liquor in the beating vat absorbs oxygen from the air, as the indigo separates from it, has, we believe, been ascertained by direct experiment; and it is also known to manufacturers, that the sunshine assists in the separation of the indigo from the liquor. But, though these facts may have been ascertained, it does not give us any positive information respecting the nature of the change which takes place in the vat; neither can we expect such information till it be ascertained what keeps the indigo in solution previous to the operation of beating. Both oxygenized and deoxygenized indigo are insoluble in water; there must therefore be some substance in the liquor capable of holding the indigo in solution previous to being beat. According to our present knowledge of the nature of white or deoxidized indigo, there is no other substance can hold it in solution except the alkalies and alkaline earths. But during such a generation and emission of carbonic acid gas, the existence of any known alkali capable of holding the indigo in solution in those vats is next to impossible, and the results prove the contrary; for while the acid is liberated, the indigo becomes more insoluble—a result which is just the opposite of what we conceive would take place were an alkali present—except we suppose that the carbonic acid is the result of the decomposition of the alkali, or alkaloid, or is evolved as already hinted, from the decomposition of a substance which is resolving itself into indigo.

Having given the opinions of several chemists upon the chemical nature of the manufacture of indigo, and hinted at the difficulties which some of these theories involve, we shall now consider the nature of indigo; and, whatever be the chemical changes which take place in the beating operation, we are certain that the indigo is precipitated in union with various other substances, rendering it very impure. The best indigo of commerce, according to several analyses, contains only 75 per cent. of pure indigo, while some of the inferior kinds do not contain above 29 or 30 per cent. Part of these impurities may be dissolved in water, by alcohol, by dilute acids, and by alkaline leys. Berzelius found those impurities

to consist, besides a little iron, of clay, lime, magnesia, and silica, of a substance resembling vegetable gluten,* which may be obtained by digesting indigo in dilute sulphuric acid (vitriol); also a *brown matter* which he terms indigo brown, and which he obtained by digesting the indigo in strong potash ley after the gluten had been extracted. He found likewise a red resinous substance, which he termed indigo red; it was obtained by boiling the indigo in alcohol, after digestion in the acid and alkali. Several experiments have been made upon the colouring properties of these substances, but the results have shown that they are incapable of being used as a dye. On the contrary, as we shall afterwards have occasion to remark, some of them being more soluble than the pure indigo, and much more easily decomposed, their presence is very hurtful, especially when the indigo is to be used as sulphate of indigo.

From the great differences in the quality of indigo, it would be of the utmost importance to the dyer to have an easy method of ascertaining its true value. This, so far as we are aware, has not yet been obtained; the various methods proposed generally imply formal analyses, which, however important they may be to the dyer, are too delicate and tedious to be generally adopted. The method universally practised in the dye-house is that of comparison—putting several samples together, and breaking and comparing their clean surfaces. The best indigo generally is of the deepest violet blue, and the finest grain, and if scratched by the nail, it presents a copper hue; but notwithstanding great care and long practice in judging of the value of indigo in this way, it often happens that the lot chosen turns out to be of inferior quality—a fact which is not discovered until it is in the vats.

The process of Berzelius, just alluded to, is to take a weighed quantity of the indigo of commerce in very fine powder, and after digesting it in dilute sulphuric acid, to filter and wash it; then digest what remains on the filter in strong potash or ammonia; filter and wash again; then boil the remainder in strong alcohol; what remains is pure indigo, and,

* Gluten is the substance which gives wheat, flour, starch, &c., the property of paste. It is a distinct vegetable substance composed of oxygen, hydrogen, nitrogen, and carbon, and it is the most nutritive of all vegetable compounds.

by weighing it, we find the per centage of real indigo in the sample.

Another process, somewhat similar, was recommended by Chevreul. He treated the powdered indigo first with water, then with alcohol, and afterwards with muriatic acid. The following is the result of his experiment, taking a hundred parts:—

Treated with water.	Green matter united to ammonia A little deoxidized indigo Extractive Gum	12 parts.	
Treated with alcohol.	Green matter Red resin A little indigo	30	—
Treated with muriatic acid.	Red resin	6	—
	Carbonate of lime	2	—
	Red oxide of iron	2	—
	Alumina	3	—
There remained,	Silica	3	—
	Pure indigo	45	—
		103	—

Although these processes give a much nearer and more certain approximation to the true value of indigo than the mere comparison of samples by the eye, still they are not direct enough, and require too much nice management to be resorted to generally in the dye-house. Those, indeed, who are most affected by a bad bargain, and ought to be most interested in any process that would enable them to avoid loss, and who have the requisite time and means to try such experiments, do not seem impressed with the importance of such inquiries.

Another method has been proposed by Dr. Dana of Lowell, United States, for ascertaining the real value of commercial indigo. He directs that ten grains of indigo, reduced to a very fine powder, be put into a small glass flask, with two-and-a-half ounces, by measure, of a solution of carbonate of soda, of from 30° to 35° of strength by Twaddell's hydrometer; after boiling for a few minutes, 8 grains of crystals of chloride of tin are to be added, and the whole boiled for

half an hour. By this means the indigo is dissolved, and the liquor appears of a yellow colour. Six grains of bichromate of potash, (red chrome,) are dissolved in 6 ounces of water; and, when the flask is withdrawn from the lamp, this solution of chrome is added, which precipitates the indigo blue, along with a trace of the indigo red, leaving the other ingredients in solution. The whole is next to be poured upon a double (weighed) filter, and the precipitate washed with 1 ounce of muriatic acid diluted with 3 ounces of boiling water, and afterwards with hot water, till nothing but water returns. Then separate, dry, and weigh the filters, and make a note of the weight of the precipitate; burn one filter paper against the other, and their difference in weight is the quantity of silica contained in the indigo. This, deducted from the weight of the precipitate, gives the quantity of pure indigo. Mr. Walter Crum, who communicated the above to the British Association, in 1841, added that carbonate of soda with protoxide of tin, dissolves indigo, and forms a yellow solution, but so slowly, that he doubts if all the 10 grains are acted upon. He thinks Dr. Dana must mean soda-ash, which contains a notable quantity of caustic soda, but a much weaker solution of caustic soda would answer the purpose.

Pure indigo, besides its great importance as a dye-drug, possesses some most important and interesting chemical properties, but which are as yet not very well understood. Some of these we shall notice before entering upon its practical value. If pure indigo be heated to about 550° Fah. it sublimes, producing a beautiful transparent vapour of a reddish-violet colour, which adheres to the sides of the vessel in which it is sublimed, or on the top of the cinder left, in long needle-shaped crystals. Mr. Crum, whose investigations have thrown great light upon the chemical nature and properties of indigo, employed for its sublimation the covers of two platinum crucibles, about three inches diameter, and of such a form that, when placed with their concave sides inwards, they were about three-eighths of an inch distant in the middle. About the centre of the lower lid were placed thinly about ten grains of indigo, precipitated from the dyer's vat, in small lumps about a grain each; then, having put on the cover, the flame of a spirit lamp was applied beneath the cover containing the indigo. The indigo immediately began

to melt with a hissing noise, which, when it had nearly ceased, the lamp was withdrawn, and the whole allowed to cool. On removing the cover, the sublimed indigo was found planted on its inner surface, and a little remained upon the charred matter, and was easily removed. In this way he obtained from 18 to 20 per cent. of the indigo employed.*

As few working men have access to platinum crucible covers to repeat this experiment, we may state, that it may be successfully repeated by taking a thin porcelain plate, or a sheet of iron or copper, with the indigo placed upon it, and covering it with a pretty large watch-glass; when the plate under the indigo is heated by a lamp, the vapours very soon make their appearance; and, towards the close, the glass appears black, owing to the coating of indigo which adheres to its inner surface. To obtain pure indigo for this experiment, the easiest method is to take a little of the yellow solution of the indigo vat. On adding to this a few drops of muriatic acid, to dissolve the salts of lime, the blue indigo falls to the bottom, and may readily be collected upon a filter, then washed and dried.

Another method has been described by T. Taylor, Esq., which is as follows:—"Any quantity of indigo is to be reduced to powder, and mixed with about half its weight of plaster of Paris. To these materials so much water is to be added, as will bring the whole to a thin paste. This is to be spread evenly upon an iron plate to the depth of the eighth of an inch, and allowed to remain exposed to the air, or to a gentle heat, until it is tolerably dry. If the heat of a large spirit-lamp be now applied to the under surface of the plate, the indigo begins to smoke, emits a disgusting odour, and in a few minutes is covered over with a dense purple-red vapour, which condenses into brilliant flattened prisms, or plates of an intense copper colour, forming a thick velvety coating over the surface immediately exposed to heat. When this ceases to appear, the heat is of course to be withdrawn; and when cold, the sublimed crystals may be readily lifted or swept off, without in the slightest disturbing the subjacent mass. The operation is exceedingly beautiful to look at, is effected in a few minutes, and any quantity of materials might be acted upon. For ultimate analysis, the sublimed indigo must be previously

* Annals of Philosophy for January, 1823.

washed with alcohol or ether. The object of the plaster is to prevent the indigo from cracking during drying." *

We have tried this experiment repeatedly, but the results did not promise favourably for the process being of practical value in the dye-house.

Another method, and of much easier practice in the dye-house than any of these given, is by Henry Schlumberger:—

"This test consists in dissolving the indigo in fuming sulphuric acid, and decolourizing the solution, which has been diluted with much water, by means of chloride of lime. As this acts only on the blue-colouring substance, and not at the same time on the various other bodies which indigo contains, the quantity of chloride of lime requisite to produce decolourization agrees, as will be subsequently seen, accurately with the amount of colouring matter.

"The operations in this experiment are as follows:—I prepare, in the first place, a portion of pure indigo or indigo blue by removing the scum which is continually formed on the blue vat, treating it with an excess of dilute hydrochloric acid, washing the deposit until all soluble parts have been removed, then drying it and preserving the indigo in well-closed bottles, in order to protect it from all changes in the moist state. In all my experiments this pure indigo serves as a standard, and for comparison with the results which the various kinds of indigo submitted to the test afford. Suppose the quantity of colouring matter in the pure indigo to be 100°, I express the value of the tested indigo by numbers which indicate the per centage of pure colouring matter. In each experiment I employ the standard indigo for comparison with that of commerce, as it is then not requisite to determine previously the amount of chloride of lime in solution; besides which, the experiment is more accurate. In this case the causes of the differences in the results depend on circumstances, which always remain the same whether the standard indigo is employed, or the indigo the degree of purity of which is to be ascertained. Twenty grains of each kind of indigo is weighed off, which must be pulverized and finely ground; half-an-ounce of fuming sulphuric acid is added, and the mixture is now rubbed together, the dish containing it being placed for four hours at a temperature of from 122° to 140°.

* Chemical Gazette, vol. i., page 115.

"Meantime as many glasses, containing about a quart, are filled with distilled water as there are sulphate solutions, and to each solution of indigo is added its equal volume of water from the glass. The liquid becomes warm, upon which they are rubbed again; water is then gradually added until the dish is full, when the whole is poured into the glass, and the dish washed with a portion of the water. Hereupon a solution of chloride of lime is prepared of 2° Twad. in strength, and a given quantity taken, say 10 graduations of an alkalimeter.

"The well-stirred blue solution of the sulphate of indigo is now measured in an alkalimeter, a tube divided into 100°, and a portion poured into a dish, well stirred, and the entire quantity of the chloride of lime contained in the measure added at once. If the liquid immediately assumes a yellow colour, it is a sign of an excess of chloride of lime, and now sulphate of indigo is added by degrees until a faint olive-green colouring has been obtained. The experiment is now repeated, and the quantity of chloride of lime which had been found necessary in the first case, added to the quantity of sulphate of indigo; so that with one single mixing, there being neither an excess of chloride of lime or of sulphate of indigo, the liquid acquires that tint at once. But when, after the first mixture, the liquid has retained a blue colour, which is a sign of an excess of the sulphate of indigo, fewer degrees of it are taken until the requisite tint has likewise been attained with a single mixing.

"When the several indigoes have been treated in this manner, the following calculation is made to obtain the true value of the indigo which has been examined; the goodness of the indigo is in inverse ratio to the quantity of sulphate of indigo employed in decolourizing.

"Suppose, for instance, it were found that pure indigo required 54 parts of its sulphate solution to be decolourized by the fixed quantity of chloride of lime, and that, on the other hand, the indigo under examination required 64 parts of its sulphate solution, then according to the proportion—

$$64 : 54 = 100 : x, \quad \frac{100 \times 64}{64} = x,$$ or equal to 84·5, which indicates the quantity of indigo blue contained in 100 parts of the indigo examined.

"It is important for the accuracy of the experiment that the pure indigo, and the kinds of indigo submitted to the test, should be equally moist, and it is therefore requisite to enclose all the samples as soon as they are taken out of the chests in glass phials, to prevent any attraction of moisture or desiccation previous to weighing. When a chest contains several kinds of indigo which exhibit slight differences in their tints, some pieces are selected which are separated into several lots, these are then powdered together, and the mean result taken as the correct one. But when, as often happens, a chest contains pieces of indigo of entirely different tints, it is best to examine the mixed sorts separately.

"I also dilute the solution both of the sulphate of indigo and of that of the chloride of lime, since the experiment in this manner is less exposed to error than with concentrated solutions. Besides, it is easier when the liquid is only faint blue to distinguish the degree of decolourization, when it must be discontinued.

"Impure water, or such as contains salts of lime, produces a more or less considerable precipitate of the blue-colouring substance mixed with sulphate of indigo; it is therefore necessary to employ rain or distilled water.

"The last stage of decolourization, or the point at which it is best to discontinue it, is the more easily ascertained, the purer the indigo, and the more complete its solution; and in this case it is evident how sensitive the reaction of the chloride of lime is on the indigo; for a yellow solution of indigo, to which chloride of lime has been added, in which, therefore, there is an excess of chloride of lime, is rendered blue by a single degree of the indigo solution, a proof that this method will indicate a half per cent. In the commercial kinds of indigo it is less easy to fix the point at which decolourization must be discontinued, for in this case the decolourized liquid assumes an olive colour, and from 2° to 3° of the indigo solution must be added to change the yellow colour into the blue.

"I have preferred the method of taking a fixed quantity of the chloride of lime and varying that of the sulphate of indigo, to that of making the sulphate of indigo a fixed quantity, and allowing the decolourizing agent to be diminished or increased, from its being possible to dilute the indigo solution with

much water, which has the advantage of rendering the degrees greater."

Another method, and of much easier practice in the dye-house, is thus given by M. Reinsch:—

Reinsch tried various modes of determining the goodness of indigo—such as the external appearance: the intensity of colour imparted to yarn by the cold vat; the quantity of indigo blue obtained by sublimation; the quantity of indigo blue deposited from the cold vat: and the specific weight. Not one of these methods, however, gave results to be relied on.

"At last," he says, "I resorted to fuming sulphuric acid, and obtained the most satisfactory results. It is necessary, however, that the indigo should be pounded very fine, and the acid should be as concentrated as possible. I must also observe, that the solution of the Java indigo, and of that indigo which I prepared in a chemical way, by treating it with acid, caustic potash, spirit of wine and water, did not possess that pure blue colour like that of the Bengal sort, although I repeated the experiments several times, and could not, therefore, determine anything with regard to the purified indigo. A dyer of great experience informed me, that for solution in sulphuric acid he prefers Bengal to the Java sort, as the latter is burnt by the acid, which is always the case when the indigo does not dissolve with a pure blue colour, but assumes a crimson hue on the sulphuric solution being poured in water.

"The mode in which I proceed is as follows:—2 grains of each sample of indigo are well pounded, mixed with four or five drops of fuming sulphuric acid, and rubbed with it until the whole forms a brown uniform mass. To this, 15 grains of sulphuric acid are added, and triturated till it produces a clear green solution, whereupon other 15 grains of fuming sulphuric acid are added; lastly, this solution is gradually mixed with 150 grains of water. Two glass cylinders of equal length and width are now divided each into twenty equal parts, and 15 grains of the sulphuric solution (which is best measured by a glass tube closed at one end) poured into one and mixed with water, till the solution is of a light-blue colour and transparent; if 15 grains of the solution do not produce sufficient colouration, a small quantity more of it is added, till the cylin-

der is filled with the light-blue solution. I generally commence with the apparently best indigo. After this the second cylinder is filled in the same way with an equal quantity of sulphuric solution of the same indigo sample and water, in order to see whether the two solutions are equal in colour. If this be the case, one of the cylinders is emptied, and an equal quantity of sulphuric solution of an inferior sample poured into it and gradually diluted with water, till the solulutions in both cylinders are perfectly alike in colour. Care is to be taken that the colouration be not too intense nor too light, it being in either case difficult to obtain both solutions of the same hue. For discovering this equality the eye will also be much assisted if the relative position of the cylinders is changed from the right to the left, or by placing them alternately before or behind one another. As soon as the colour of both is thus found to be equal, the quantity of water is examined which has been poured into the second cylinder. Supposing now that 15 grains of sulphuric solution have been employed in either of the cylinders, but the quantity of water which produced the equal colour was in the first or standard cylinder 20 parts, and in the second only 15 parts, then the sample of which the latter solution was made will contain $\frac{5}{20}$ths, or one quarter less of colouring matter.

"This method is so easy and convenient, that everybody can avail himself of it. All that is required is to keep ready a certain quantity of indigo solution of a known quality as standard solution, and then to prepare a sulphuric solution of the indigo to be tested.

"The above-described method may even be made more accurate if longer glass cylinders are used, so that the per centage quantities may be indicated. The glasses must then be divided in 100 parts. The larger the degrees are, the more accurate will the results be.

"I have yet to add some observations with regard to an adulteration practised on the indigo, and which is of importance to the druggist. Each large indigo-chest contains a quantity of dust, which is said to amount sometimes to 8 or 10 pounds. This dust is an artificial product, composed of starch or white lead and powdered indigo, and is put in the chest in order to increase its weight."

Another process of testing the value of indigo has been

recommended by Dr. Bolley, depending also upon the decolourizing by chlorine, by a method which insures the constancy of the chlorine, this is done by using hydrochloric acid and chlorate of potash. A given quantity of indigo, say 100 grains, is ground into powder, and converted into sulphate of indigo by adding to the 100 grains about $2\frac{1}{2}$ ounces of the strongest sulphuric acid, and allowing it to stand for six or eight hours. The whole is now put into an evaporating basin or flask, with about one pint of water, and one quarter of an ounce, by measure, of hydrochloric acid, and brought to boil. A solution of chlorate of potash is now made in 100 measures of water by alkalimeter, (which is added to the indigo solution), the blue liquor passes into green, brownish-green, and lastly into red, when the operation is finished. A little experience will show the exact time to stop. The amount of chlorate solution taken to effect this is noted, and a standard solution being made, the relative value of indigo will be easily ascertained.

Another method of testing the value of indigo has been recently recommended by Dr. Penney of the Andersonian University, Glasgow, based upon the circumstance that indigo blue, in presence of hydrochloric acid, is decolourized by bichromate of potash. Ten grains of the sample, in very fine powder, are dissolved in 2 drachms, by measure, of fuming sulphuric acid, forming sulphate of indigo. After standing several hours, to insure complete solution, it is diluted with a pint of water, and the whole well stirred, after which there is added $\frac{3}{4}$ of a volume ounce of hydrochloric acid. Seven and a-half grains of dry and pure bichromate of potash are now dissolved in water—the whole solution to be equal to 100 measures of an alkalimeter; this is added drop by drop to the sulphate of indigo, until the blue colour disappears, and the colour of a drop of the solution put on a white plate or paper be orange-brown, having no green or blue tint. The number of graduations required to effect this is noted. Dr. Penney found that $7\frac{1}{2}$ grains bichromate of potash were equal to 10 grains pure indigo, so that every 10 graduations of the solution taken to decolour the sulphate, are equal to 1 grain of pure indigo, or 1 graduation to a per cent. of indigo.

Commercial Indigoes.—The following description of commercial indigoes is taken from Dumas' Lectures upon Agriculture:—

"*Indigoes of Commerce.*—The indigoes of commerce have been described in a very able manner by M. Chevreul. The following details are extracted from his work:—They are sometimes in small, light pieces, of a violet-brown colour, and sometimes in cubical loaves. These loaves may be considered good, when they assume a copper-coloured aspect on friction with any hard and smooth body—when there are no cavities found in their interior, presenting a series of brown or whitish-coloured streaks—and, lastly, when they are free from fissures externally. If they are of a blue instead of a violet colour, it is a proof that they contain more or less of the yellow matter. The presence of this matter in large proportions, tends by its admixture to convert the blue into a green, and also neutralizes the colour of the red matter of indigo. An obscure dark brown or dirty-green colour indicates, in general, that the indigoes have undergone some deterioration in their preparation or during their transport. Indigo is destitute of odour, provided it has undergone no alteration by heat and moisture. Indigoes are classified into different kinds, according to the country in which they are prepared, or according to their colour.

"First, Indigoes prepared in Asia—they are from Bengal, Coromandel, Madras, Manilla, and Java:—

"*Bengal Indigoes.*—The trade in this indigo is chiefly carried on in Calcutta, and through the medium of the East India Company; its varieties are very numerous. The principal, commencing with those of the best quality are:—1° The superfine or light blue. This is in a cubical form, light and friable, soft to the touch, of a clean fracture, and giving a beautiful copper colour on being rubbed with the nail. 2° Superfine violet. 3° Superfine purple. 4° Fine violet, in colour a little less brillant than the superfine, and rather heavier. 5° Fine purple violet. 6° Good violet, somewhat heavier than the fine violet. 7° Violet red. 8° Common violet. 9° Fine and good red, heavier than the preceding, colour bordering decidedly on red. 10° Good red, of a firmer and more compact structure. 11° Fine copper-coloured, redder and more compact still. 12° Middling copper-coloured. 13° Ordinary and low copper-coloured; this is of a copper-coloured blue or red, somewhat difficult to break.

"*Coromandel.*—Those of the best quality correspond to the

middling Bengal indigoes, and are met with in square masses, having an even fracture, but are more difficult to break. The inferior indigoes are heavy, of a sandy feel, having a blue colour bordering on green or gray, or even black; often in very large squares, and covered with a slight crust or rind of a greenish-gray colour. These are the most difficult to break of all the indigoes of commerce.

"*Madras.*—They have a grained rough fracture, and are of a cubical figure. The superior qualities have no *rind;* in figure they somewhat resemble a *hat*, and are more light and friable than those of Coromandel. These indigoes, when of the best quality, have great lightness, but are not equal to the superfine blue of Bengal. The middling qualities have a very slight copper colour. The colour of the inferior qualities is a dark or muddy blue, black, or even gray, and greenish.

"*Manilla.*—These present the mark of the rushes upon which they have been dried. They are of a finer consistence and lighter colour than are the indigoes of Madras, but not so fine as the indigoes of Bengal. The better qualities are often in flat and elongated masses, somewhat porous, and consequently light. The middling qualities are of a violet colour, but they are inferior to the violet of Bengal.

"*Java.*—In flat, square masses, sometimes of a lozenge shape. The superior qualities appear to the sight as fine as the blue, violet, or red indigoes of Bengal; but they are not so in reality.

"2°. Indigoes prepared in Africa. They are from Egypt and Senegal:—

"*Egypt.*—The superior qualities of Egyptian indigo are superfine and fine violet blues. They are light, but their structure is not very fine, and they often contain sand. The squares are rather flatter than those of Bengal.

"*Senegal.*—They are of good quality, but they contain more earthy matter than any other indigoes in the trade.

"3°. Indigoes from America; those of Guatimala, Caraccas, Mexico, Brazil, Carolina, and the Antilles:—

"The indigoes of *Guatimala*, of the *Caraccas*, and of *Mexico*, are of various kinds. The best are of a bright blue colour, remarkably light and fine. These indigoes are esteemed equal to the best Bengal. The inferior qualities are of a violet colour, but, in general, are more mixed than the Bengal kinds.

"*Brazil.*—These indigoes are in small rectangular parallelopiped masses, or in irregular lumps, of a greenish-gray colour externally, and having a smooth fracture, a firm consistence, and a copper-coloured tint of greater or less brilliancy.

"*Carolina.*—In small square masses, having a gray exterior. The best qualities have a dull copper colour, bordering on violet or blue. The common qualities are almost always of a greenish-blue; they are rarely found of a copper colour.

"The principal varieties of indigo in commerce are the Bengal, the Caraccas, the Guatimala, the Madras, and the Manilla.

"Besides the numerous shades already described, we should also be on our guard against certain defects, of greater or less consequence, and which depend on causes acting either on the indigo when already prepared, or else occurring during its preparation. The following are some of the characters to be borne in mind:—The large or small fracture: squares of indigo reduced, by accident, into lumps of variable size. Fragments: squares reduced into irregular pieces, and fine enough to be passed through a sieve. Sometimes, also, we meet with squares which are readily broken, and which present a whitish kind of mouldiness in their interior. Gritty lumps, throughout which are points presenting the appearance of granite. Streaky masses, in which are layers of various shades of blue, placed one above the other, in the same square. Pieces of a scorched appearance, which, on being sharply rubbed between the hands, are ground into small fragments, nearly black in colour. Sandy lumps, in the interior of which the eye can detect shining specks, which are nothing more than sand."

Pure indigo, whether obtained by sublimation, or other chemical means, is of a deep blue, approaching to violet. If scratched or rubbed, it has a strong copper hue, and a metallic lustre. It has neither taste nor smell, and is remarkable for its neutral properties. It is insoluble in water, alcohol, ether, alkalis, and dilute acids. Strong sulphuric acid dissolves indigo readily, and forms with it a purple-blue solution. Its chemical composition is, according to Mr. Crum and M. Dumas:—

16 Carbon.		32 Carbon.
5 Hydrogen.	or double,	10 Hydrogen.
2 Oxygen.		4 Oxygen.
1 Nitrogen.		2 Nitrogen.

The double proportion is preferred, as it agrees better with some of the reactions to be afterwards explained.

The chemical qualities, and some of its reactions, have been extensively studied. If blue indigo be brought into contact with substances having a strong attraction for oxygen in the presence of an alkali, the indigo is reduced to the white state, and becomes soluble in the alkali; this, as is well known, is the principle of the blue vat. The following matters all reduce blue indigo to white:—

Protoxide of tin,	The sulphurets of potassium,
Protoxide of iron,	Sodium,
Sulphuret of arsenic,	Calcium,
Phosphorus,	Sugar,
The phosphites,	Starch,
Sulphites,	Tannin.

Salts, which yield oxygen, as those of copper, turn white indigo to blue, and the copper is reduced to the suboxide. Water having carbonic acid, also oxidizes white indigo. Indigo white is a crystalline solid, having a fibrous silky lustre, tasteless, without smell, and heavier than water; it is insoluble in water, but soluble in alcohol and ether.

White indigo, well dried, may be kept in the air for several days without change, but if moist it soon becomes blue; when heated it becomes purplish-blue. The composition of white indigo is still, to some extent, an unsettled question. According to the most generally received opinion, white indigo is blue indigo with less oxygen, sometimes called deoxidized indigo, but Dumas considers it as blue indigo, with an equivalent more of hydrogen:—thus we have

By the Common Theory.		By Dumas's Theory.	
Carbon	16	Carbon	16
Nitrogen	1	Nitrogen	1
Hydrogen	5	Hydrogen	6
Oxygen	1	Oxygen	2

Dumas supports his view of the matter by reference to

many vegetable organic substances which he thinks comport themselves in a similar manner, and gives a series of formulæ of compounds, which by analogy he connects with indigo. Thus:—

	C.	H.	O.	H.	N.
Blue indigo (double atom).....	32	10	2	0	2
White indigo.....	32	10	2	2	2
Acetyle.....	8	6	2	0	0
Aldehyde.....	8	6	2	2	0
Benzule.....	28	10	2	0	0
Oil of Bitter Almonds.....	28	12	2	2	0
Cinnamule.....	36	14	2	0	0
Oil of Cassia.....	36	14	2	2	0

Here we observe a series of compounds differing more widely from each other than white and blue indigo, and only caused by having 2 proportions more of hydrogen. A like analogy is carried out between compounds of indigo with other bodies, and compounds of other organic vegetables, which, however, we must pass over.

Liebig's view of the reaction of indigo, and its relations to other bodies, differs from that of Dumas. He considers, as the result of careful and extensive investigation, that indigo contains a salt radical (page 33) which he terms *anyle*, and which is composed of C_{16} H_5 N. This, it will be observed, is indigo without any oxygen. He then considers that white indigo is the *hydrated* protoxide of this base or radical, and that blue indigo is the peroxide. Thus:—

	C.	H.	N.	O.	Water.
Anyle.....	16	5	1	0	0
White indigo.....	16	5	1	1	1
Blue indigo.....	16	5	1	2	0

Taking double proportions for comparison:—

Anyle.....	32	10	2	0	0
White indigo.....	32	10	2	2	2
Blue indigo.....	32	10	2	4	0

This view of the matter, which we think most consistent with fact, and to which we may have occasion to return in describing the vat, can be supported by analogies in the same manner as the other view. Indeed, most of the colouring

principles of vegetables, such as madder, annotta, archil, &c., exist in the plants as colourless bases, and become coloured by the absorption of oxygen.

M. Pressier, who has been very fortunate in his researches into vegetable colouring matters and bases, thinks that he has found a decisive argument in favour of Liebig's view, in the fact that blue indigo, sugar, and potash react together, and form white indigo. He therefore considers it very improbable that indigo should extract hydrogen from water, at the same time that the oxygen of the water would combine with the hydrogen of the sugar to reproduce water. Dumas, however, observes upon this, that there is no necessity for supposing water to be decomposed, as the hydrogen of the sugar may combine directly with the indigo blue and form indigo white. These views of the question show that the subject is still one of difficulty, and is full of interest; and that the daily experience of the dyer, were the results carefully observed, might afford important aid towards the solution of some of those vexed questions of chemical science.

If indigo be thrown into fused hydrate of potash, its blue colour disappears; it dissolves, and is partly decomposed along with the water of the alkaline hydrate; hydrogen, and ammoniacal gases are evolved, while carbonic acid, and another acid, named valerianic acid, having properties similar to acetic acid, are formed, and combine with the potash. By digesting this mixture with a little sulphuric acid, the alkali combines with it, and the new acid crystallizes. This acid combines with alkalis, and other bases, and forms a very interesting series of salts.

If indigo, in fine powder, be added to nitric acid, diluted with seven or eight times its weight of water, and a gentle heat be applied, it dissolves with effervescence, forming a yellow liquid. After standing a little, this liquid may be decanted from any resinous matter formed during the process, and concentrated by evaporation, and speedily there will be found deposited a quantity of yellowish-white crystals, having a sourish-bitter taste, and requiring about 100 parts of cold water for their solution. This was formerly termed indigotic acid, but is now called anilic acid, from the species and name of one of the plants which yield indigo. It combines with all known bases, forming salts, which have generally a yellow

colour. It gives a blood-red colour to solutions of the persalts of iron.

If indigo be added to strong nitric acid, and heat be applied, it quickly dissolves, evolving a great quantity of nitrous gas. On allowing the liquid to cool, a large quantity of semi-transparent yellow crystals are formed, having a very bitter taste. This is what was, till lately, called carbazotic acid; but this name has been changed to picric acid.

To procure it in a purer state, the crystals obtained by the above operation are to be washed in cold water, and then boiled in water sufficient to dissolve them; next filtering the liquid and allowing it to cool. The acid again crystallizes in brilliant yellow prisms. The acid may also be obtained by the action of nitric acid upon anilic acid.

Picric acid is very permanent in its constitution. When fused in chlorine or with iodine, it is not decomposed, nor does a solution of chlorine affect it. Cold sulphuric acid has no action upon it, but dissolves it when hot. Boiling hydrochloric acid does not act upon it, but nitro-muriatic acid (*aqua regia*) dissolves it with difficulty. It acts like a strong acid upon metallic oxides, dissolving them, and forming peculiar crystallizable salts. These are yellow; they detonate strongly when sharply heated, and also by percussion, particularly the salt formed with potash. When a little of it is gradually heated in a glass tube, it first fuses, and then suddenly explodes, breaking the tube to pieces. Care is necessary in making this experiment, as the fragments of glass may injure the face.

This acid is an excellent test for the presence of potash in any fluid, a solution of it in alcohol producing a bright yellow crystalline precipitate, even in a diluted solution of the alkali. It is thus more sensible than the chloride of platinum, commonly employed for the detection of potash; for that re-agent does not produce a precipitate in dilute solutions.

When indigo is acted upon by very diluted fuming nitric acid, it unites with two atoms more of oxygen, and is consequently converted into a new substance, which has received the name of *isatine*. This substance under the influence of alkalis, absorbs one equivalent more of water, and assumes an acid character, and is termed *isatinic acid*. This acid combines with other substances forming a series of compounds, the nature of which is not yet very well known.

Chromic acid has a similar action upon indigo as nitric acid.

When indigo in the dry state is brought into contact with dry chlorine, no chemical action is observed; but when indigo, suspended in water, is subjected to the action of chlorine, several new products are formed. When the fluid thus acted upon is distilled, a fluid product in minute quantity passes over with the distilled water, and collects under it in the receiver in the form of white scales, which has been termed *chlorindoptin*. It is sparingly soluble in water, but copiously in alcohol. The substance which remains in the retort is found to be a mixture of several new products. On being dissolved in boiling alcohol, it yields, on cooling, red prismatic crystals of a bitter taste, and very insoluble in water; this has been named *chlorisatin*. It dissolves in a solution of caustic potash, producing a red colour. The salts of lead give with this solution a yellow precipitate, which becomes a fine scarlet by standing. The salts of copper, (blue-stone,) &c. give a brown, which becomes blood-red by exposure to the air. In the alcoholic solution, another substance is found having an equivalent more of chlorine than that named above; this is termed *bichlorisatin*. Its properties, however, are analogous to those of chlorisatin; its solution in potash gives a yellow precipitate with the salts of lead, but does not alter by exposure to the air; and with the copper salts it gives a yellowish-brown, which passes to blood red. When chlorine is passed through a solution of chlorisatin, another substance named *chloronile* is formed. This crystallizes in scales of a brass-yellow colour, and when dissolved by potash gives a beautiful purple colour.

If indigo in powder be added to a solution of caustic potash of specific gravity 1·35 (70 Twaddell) and boiled, an orange-yellow salt is formed. The solution of the boiled mass becomes blue in the air from absorption of oxygen, like a solution of white indigo, and blue indigo precipitates.

Besides the compounds resulting from the action of nitric acid and chlorine upon indigo, there are several others which from their true characters being still little known, we have not thought it necessary to enumerate. Some practical dyer may indeed be inclined to ask, what those already noticed have to do with dyeing? We are sorry that with respect to some of them, we cannot give any satisfactory answer to the

question; but the same question was asked, when chemists first intimated that chromic acid produced yellow salts when combined with lead; yet this simple hint has completely revolutionized various departments of dyeing; and the action of chromic acid upon indigo, as already observed, has been both a source of annoyance and advantage to the dyer. Previous to the use of alkaline solutions of lead, dyers seldom could get an evenly *chrome* green; the chromic acid being set at liberty acted upon the indigo which was upon the yarn, destroying in part the blue colour, after which the green was all light-yellow *blains*. These annoyances are still felt where the new process of working the lead solution with an alkali is not practised. But this same action of chromic acid upon indigo has been taken advantage of by calico printers, when they want a white pattern on a blue ground.

Previous to the introduction of bichromate of potash for this purpose, the calico printers were, to a certain extent, limited. Thus:—

The pattern is printed upon the cloth with the oxide of a metal which yields its oxygen easily to other substances, such as copper and zinc; the goods are afterwards dyed blue by passing them through the vat; but the parts upon which these metallic salts are printed, resist the dye, by yielding their oxygen to the indigo, a process which will afterwards be described, so that the piece when finished is a blue ground with a white pattern. But after the blue vats have been wrought for some time, they cannot be used for this purpose, owing to the weakness of the dye, and the consequent length of time necessary to produce the required shade. So that these *resist pastes* are in a manner washed off, and the pattern spoiled. Now, in place of throwing out as useless, vats thus exhausted, as was formerly done, the cloth is dyed blue without resists, and after being slightly scoured and washed, it is passed through a strong solution of chromate of potash, and dried in the shade; the required pattern is then printed on the cloth with a mixture of oxalic and tartaric acids made into a paste by gum or clay. The potash in union with the chromic acid is taken up by these acids, and the chromic acid being set at liberty, acts on the indigo, and a white pattern is produced. This ingenious process was discovered by a German chemist.

The following table exhibits the composition of those substances which we have briefly described as resulting from the action of nitric acid and chlorine upon indigo. It may be required for reference:—

Name.	C.	H.	O.	N.	C.	Water.
Indigo	16	5	2	1	0	0
Isatine	16	5	4	1	0	0
Isatinic acid	16	5	4	1	0	1
Anilic, or indigotic acid	14	4	9	1	0	1
Picric, or carbazotic acid	12	2	13	3	0	1
Chlorindoptin	16	4	2	0	4	0
Chlorisatin	16	4	3	1	1	0
Bichlorisatin	16	4	3	1	2	0
Chloranile	6	0	2	0	2	0
Valerianic	10	9	3	0	0	1

The only substance which dissolves indigo, without destroying its colour and composition, is highly concentrated sulphuric acid. For this purpose the fuming acid of Nordhausen is preferable, (page 92,) as when other acid is used, a greater quantity of it is required. The substance formed is popularly known by the names of sulphate of indigo, Saxon blue, China blue, and extract of indigo. The action of sulphuric acid upon indigo is found to be something more than a mere solution: a chemical combination, in definite proportions, results, forming two distinct substances, differing considerably from each other in their properties. These two compounds were discovered and described by Mr. Crum, and called by him *cerulin* and *phinacin*, from their colours—the former blue, and the latter purple. They have been since named sulph-indylic acid, and sulpho-purpuric acid. The former, which constitutes the blue principle of Saxon blue, is formed most abundantly when the sulphuric acid is sufficiently strong and abundant, and other proper means attended to. Its composition is found to be one atom of indigo combined with two of sulphuric acid. The other is the principal product when the indigo preponderates. It is of a purple colour; and when the solution is diluted with water, it precipitates. Its composition is found to be equal to one atom indigo to one of sulphuric acid.

From the nature and properties of these two substances, it is evident that every care should be taken to convert the

indigo into sulph-indylic acid, and to avoid the formation of sulpho-purpuric acid. The circumstances under which this latter acid is formed are—first, too little acid in proportion to the indigo, and secondly, too little time allowed for digestion. The general proportions used by dyers vary from three to five pounds of acid to the pound of indigo. This is by far too little, and occasions a considerable loss of indigo by the precipitation of the sulpho-purpuric acid, when the solution is diluted with water. Close observation shows that it requires from six to eight pounds of concentrated sulphuric acid to convert a pound of indigo into blue sulph-indylic acid. From some investigations lately made by M. Dumas, indigo requires even a larger proportion of acid to convert it into sulph-indylic acid. He recommends no less than fifteen parts of acid to one of indigo. This quantity, however, we have found to be of no advantage in practice, but rather the opposite, particularly when the acid is to be neutralised before the indigo solution is used, which is the general custom in dyeing cotton.

We have said that the second circumstance under which sulpho-purpuric acid is formed is that of too short time being given for the indigo and acid to digest. When indigo is first put into the sulphuric acid, there seems to be an immediate solution; but if a drop be spread upon a window pane, it appears of a dirty-green colour; and if allowed to stand for a little upon the glass, a yellowish-coloured liquid begins to run from the blue mass, occasioned, no doubt, by the acid absorbing moisture, and separating itself from the indigo, and clearly showing that the change upon the indigo by the acid is not an immediate effect. The more impure the indigo, the darker and greener appears the substance when put upon the glass. After the mixture has stood two or three hours, and tried in the same manner, it appears of a reddish-purple colour—the principal compound existing now in the solution being sulpho-purpuric acid. As the liquid stands, it begins to assume a violet shade, and finally passes to a deep rich blue. But dyers seldom obtain it in this state: in their hands it generally has a reddish tinge. Mr. Crum found that when the solution is diluted with water, after the colour has become of a bottle-green, the action of the acid is stopped, and sulpho-purpuric acid only is formed. But there are other means by

which the action of sulphuric acid upon indigo may be stopped, than by directly diluting the solution with water. As already intimated, it is only the highly concentrated sulphuric acid which converts indigo into sulph-indylic acid. Now, dyers not unfrequently alter the strength of their acid by the process of mixing and preparing their *chemic*, (the technical name for sulphate of indigo.) This is very generally done in an open wide-mouthed vessel, which is allowed to stand uncovered, probably in the midst of the steam and vapours of the dye-house; or, in some cases, the vessel is put into a boiler, or tub with boiling water. By these injudicious means, the sulphuric acid, which absorbs water very rapidly, is diluted below the necessary strength for dissolving indigo; and the result is, the formation of sulpho-purpuric acid, instead of sulph-indylic acid, which is the real substance wanted.

Another cause of the stopping of the action of the acid by dilution is, from the indigo. Ground indigo absorbs a quantity of moisture; and if it be not thoroughly dried previous to putting it in the acid, the acid is too much weakened to effect the formation of the substance required.

There are other causes by which the preparation of *chemic* is injured. Sometimes the acid and indigo are mixed together at once, and by this means the heat evolved is sufficient to decompose the impurities of the indigo. Part of the acid also suffers decomposition, and a great quantity of sulphurous acid gas is given off—so much, indeed, that the head cannot be held above the vessel for any length of time without injury. Another practice is, for the sake of quickening the operation, to place the vessel upon the flue in the stove, and keep the solution for hours at a heat upwards of 300° Fah. The gas given off in these cases is sometimes so great as to destroy the colours of goods hanging in the stove. Indigo submitted to such treatment is seldom found good: often its appearance on white paper or glass (which is a general method of testing the quality of sulphate of indigo) is a blackish-green—sometimes a dirty purple—seldom the fine blue violet—scarcely ever the beautiful blue.

Although the sulpho-purpuric acid is precipitated when water is mixed with the solution of sulphate of indigo, and is insoluble in dilute acids, it is, when freed from the sulphuric acid, soluble in distilled water; but if any substance be in

the water—and common spring water is never pure—it is less soluble. It dissolves in alkalis, and in solutions of the alkaline earths, giving a blue colour, of greater or less purity, according to the nature of the solvent.

We have found the following method of preparing sulphate of indigo, in quantities for use, very satisfactory:—The indigo is reduced to an impalpable powder, either by grinding in a mortar or a mill, and completely dried, by placing it upon a sandbath or flue for some hours, at a temperature of about 140° or 150° Fah. For each pound of indigo, six pounds of highly concentrated sulphuric acid are put into a large jar, or earthen pot, furnished with a cover. This is kept in as dry a part as possible, and the indigo is added gradually, in small quantities. The vessel is kept closely covered, and care taken that the heat of the solution does not exceed 212° Fah. When the indigo is all added, the vessel is placed in such a situation, that the heat may be kept at about 150° Fah., and allowed to stand, stirring occasionally, for forty-eight hours. These precautions being attended to, we have uniformly found that any failure occurring was clearly traceable to impurity of the indigo, or weakness of the acid used.

The dyer now very seldom prepares his own sulphate of indigo; it is manufactured for him, and sold in the market as *indigo extract*, which, when properly prepared, is a superior article to that prepared by himself. The following is the process of its manufacture:—The indigo is dissolved in the sulphuric acid as described; it is then diluted with hot water—distilled water is best; the whole is put upon a filter of woollen cloth, by which means the insoluble impurities of the indigo are separated. The blue solution which has passed through the filter is transferred to a leaden vessel, and evaporated till reduced to about three gallons for every pound of indigo used. There is then added about 4 lbs. of common salt to the pound of indigo, and the whole is well stirred. The sulpho-indylic acid is thus precipitated, and the whole is again thrown upon a similar filter of woollen cloth; the extract remains upon the filter, and, when sufficiently drained, is ready for the market. Some makers add a little potash or soda, which may be advantageous, and a little ammonia gives the extract a beautiful bloom. A pound weight of good indigo should yield 14 lbs. of extract. The adulterations in this solution are various.

Some of the insoluble matter is occasionally added, but not often, as it deteriorates the appearance of the *extract.* The addition of a little lime or barytes, gives an insoluble precipitate, which adds weight to the extract; but all practices of that kind react upon the maker; for, although the dyer may not have methods of testing his stuff, he very soon ascertains its working value by experience.

The extract of indigo is used in the dye-house in the same way as the sulphate was used before this method of preparation was adopted. The general term of *chemic* is applied to both, and chemic blue is used in various operations. For dyeing silks and woollens blue, the extract is simply diluted, and the goods merely passed through it; but this method cannot be adopted with cotton, as its fibres have no affinity for sulphate of indigo. But although not used for dyeing blue upon cotton, it is extensively used for dyeing green upon light goods of that material. When the cloth is dried from the sulphate of indigo solution, the acid of the chemic must be neutralized: for this purpose the chemic is prepared differently. The extract is put into hot water—the exact quantity is not material—and well stirred; to this solution a quantity of pounded chalk or whiting is added gradually, until the acid is exactly neutralized; this is a nice operation, and requires great care on the part of the operator; for, were the acid property to prevail in the least, it would destroy the yellow upon the cloth to be dyed green; and were the alkaline matter predominant, it would brown the yellow, and the green would assume a blackish-olive shade. Thus the beauty of the colours depends upon the dyer being careful to stop just at the turning point. The only method employed by dyers for determining the point of neutrality is the taste; and this, from many circumstances which we need not enumerate, is liable to error; and when the dyer is deceived, the results are very annoying, and also expensive. Were very delicately prepared blue and red litmus-papers used, the results would be much more certain. However, the reader may be astonished when we inform him, that failures from this source are very seldom. Some dyers use carbonated alkalis, such as soda and potash, to neutralize their acid; and no doubt when any of these are used, the sediment at the bottom is much less; but we have always thought that owing to the salts formed by these

alkalis being dissolved in the blue solution, the green colour is not so good, especially when *bark* is the yellowing substance.

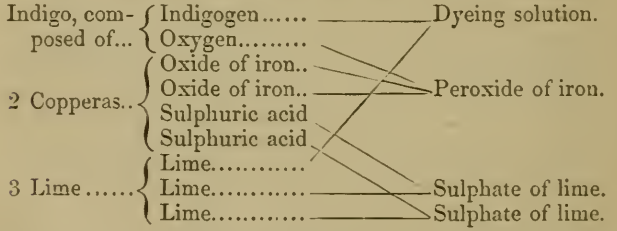
The process of dyeing greens by this sort of prepared chemic is as follows:—The goods, after being well boiled and washed, are put through a dilute solution of pyrolignite of alumina of specific gravity 1·035, that is 7 of Twaddell, and washed from this through hot water; they are then wrought through a decoction of *quercitron bark*, or *flavine*. When sufficiently yellow for the shade of green required, they are then wrought through a quantity of chemic mixed with cold water; wrung from this and dried. If fustic is the yellowing substance used, alum is a better mordant.

The greatest portion of the indigo imported is used for dyeing blue by means of the blue vat. We have already mentioned that indigo is insoluble, except in strong sulphuric acid; but if it be by any means deprived of an atom of oxygen, (according to the common theory,) it is soluble in alkalis. It may be said, that, according to the law of definite proportions described in our first article, it cannot be indigo with an atom less of oxygen. Neither is it; and we see that it has different properties from common indigo, for it is soluble even in weak alkalis; has a powerful attraction for oxygen; and is of a white colour. This substance has been termed *indigogen*, and it may be observed, that the nature of the blue vat depends upon the introduction of substances capable of extracting oxygen from the indigo, and converting it into *indigogen*. The substances generally used for this conversion are the protoxides of iron and tin, orpiment (sulphuret of arsenic,) and organic substances. These last produce the desired effect by their decomposition, such as in the woad vat, where, by the fermentation of the woad and madder, the oxygen is extracted from the indigo, which is thus converted into indigogen. The indigogen is dissolved, as it forms, by the potash put into the vat.

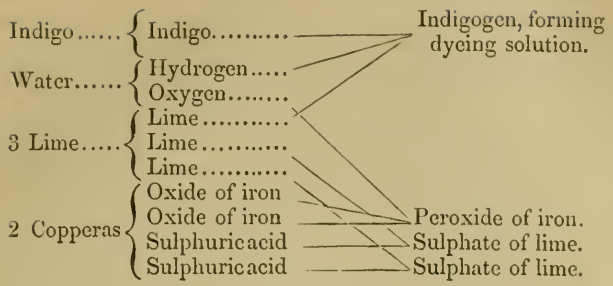
What is termed the common blue vat, or lime vat, is made up with indigo, lime, and sulphate of iron (copperas). But before describing the nature of this vat, it will be necessary, at the risk of a little repetition, to refer to the properties of oxide of iron (page 152.)

The protoxide of iron, especially when in contact with moisture, has a strong attraction for more oxygen so as to pass into the peroxide. When the sulphuric acid of copperas is neutra-

lized by an alkali, the iron is left in the state of a protoxide. The blue vat is made up by putting lime, copperas, and indigo into a vessel filled with water, and stirring occasionally for a day or two, when the indigo is dissolved. Thus:—When finely ground indigo is put into a vat with a mixture of lime and sulphate of iron, the first action which takes place is the decomposition of the metallic salt; the acid, which is in union with the iron, combining with a portion of the lime, forms sulphate of lime and oxide of iron. The detached oxide of iron extracts more oxygen from the indigo, converting it into indigogen, (white indigo,) and the peroxide of iron and the sulphate of lime thus formed are precipitated, forming what is technically termed *sludge*. The remaining portion of lime dissolves the indigogen, and forms with it the solution required. The following diagram represents this action and the results more clearly, and gives one view of the theory of the blue vat:



It will be observed that this theory of the vat is founded on blue indigo being an oxide, but, according to the view which Dumas takes of the constitution of indigo, the action which takes place in the vat will be somewhat different from that given above. When the lime combines with the acid of the copperas, the iron decomposes a portion of water combining with the oxygen, and the hydrogen combines with the indigo forming indigogen, which may be represented as follows:—



This theory is equally, if not more beautiful, than the former, but in some cases it is scarcely reconcileable with our chemical experience. When the goods are put into the vat, the dissolved indigogen combines with them, and when brought into contact with the air, according to the former theory, the indigogen combines with oxygen, for which it has a strong disposition, and blue indigo is formed, and remains combined with the cloth, but according to the latter theory, the blue indigo is left in combination with the cloth by the hydrogen combining with the oxygen of the atmosphere, and forming water. The supposition that hydrogen should combine with the free oxygen of the air, and form water so rapidly under such circumstances as mere exposure, is somewhat anomalous, but this is no reason for rejecting it. If a mixture of copperas and lime be put into a bottle with distilled water, the water is not decomposed; the lime combines with the acid, which, along with the iron, is precipitated, and if the air be completely excluded, the iron remains as a protoxide for days; indeed, the change from a protoxide to a peroxide, is so slow, that a long time elapses before it is appreciable; but if indigo be added, even after the mixture has stood for some time, the action of the common vat proceeds. This, according to Dumas's theory, gives a beautiful illustration of relative affinities. Before the indigo is introduced, the attraction of the iron for oxygen is about equal to that of the hydrogen, which holds it in combination as water, but when the indigo is introduced, although its attraction for hydrogen must be very weak, as it requires the nicest management to get that compound isolated, still it is sufficient to disturb the equilibrium with which the

oxygen was held by the iron and hydrogen, giving the former the mastery. Whether the presence of an alkaline substance has any effect of inducing, if we be allowed the term, the formation of indigogen, we cannot pretend to determine; but it is never formed in the vat without the presence of some alkaline substance to dissolve it the moment it is formed. This circumstance also explains that the alkali having also an affinity for indigogen, may assist the reaction in the vat.

We would recommend the reader to re-peruse the remarks upon the salts of iron, in connection with these on the blue vat, in order that he may be better able to appreciate them, and especially to understand what ought to be the properties of good copperas from the part it is required to play in the vat; also why it is that the quality of the copperas makes so great a difference in the working of a blue vat.

There is one serious annoyance often experienced in working the vat, technically called *swimming;* that is the precipitate not settling down, the goods come in contact with it to the serious injury of the colour. This may be occasioned by several circumstances. Should the copperas have an excess of acid, either from its being crystallized out of an acid solution, or from its having sulphate of alumina in it, (as described at page 155,) it will form a sulphate of lime, which will not precipitate so quickly as that formed by the decomposition of the copperas; but the prevailing cause of a floating vat is excess of iron and lime. Let the dyer take a solution of copperas or protosulphate of iron, and one of persulphate, and add to each a sufficient quantity of lime to precipitate the iron, he will find that the peroxide of iron will precipitate rapidly and completely, and that the protoxide will precipitate slowly and incompletely. The same phenomenon takes place in the vat when lime and copperas are added; sulphate of lime and protoxide of iron are formed, and if there be not enough of indigo to convert the protoxide of iron to the state of peroxide—in which state it precipitates easily—the protoxide will remain floating for a long time. Hence the floating vat—the only cure for which is the addition of a little indigo, or of a substance that will peroxidize the iron. When vats become weak, great care should be taken not to add an excess of copperas. We have seen a little soda added to a floating vat as a cure, and if the evil consisted in the quantity of the

copperas, this mode of cure might be successful, but not otherwise. A floating vat is sometimes caused by using improper lime. When slaked lime lies exposed for a short time to the air, and more especially in a work such as a dye-work, it absorbs carbonic acid, and becomes converted into chalk, and this put into the vat is very deleterious in other respects, besides causing *swimming*. The lime used for the vat should *always be newly slaked*. This is a necessary precaution, as the practice is too often otherwise than is here recommended.

When the paucity of indigo in the last stages of a vat causes floating, a small portion of a copper salt may be of service, as this oxide will give up a part of its oxygen to the iron, becoming a suboxide; or it will oxidate a portion of the indigo in solution, and this would react in turn upon the iron. The property of this and some other metals for neutralizing the effects of iron in the vat has already been noticed; but it may be more apparent by thus referring to it here, and it may be still further enforced in connection with that branch of calico printing called *resist-work*, indicated at page 295, and which may be thus further described:—A certain preparation, the best we believe is the sulphate of copper or zinc, is mixed either with flour paste, with gum, or with pipe-clay and gum, and printed on the calico, of any pattern that may be desired; when this is sufficiently dry, the goods are dyed in the blue vat; those parts of the piece which are printed with the copper or zinc will not be dyed blue, because the deoxodized indigo becomes oxygenated the moment it touches the copper, which yields its oxygen to the indigo, and occasions it to become insoluble, and consequently incapable of forming a dye. According to Dumas's theory, the hydrogen, in combination with the indigo, unites with the oxygen of the copper and forms water—the results are alike in both.

Before concluding this article, we may inform the general reader that, in print-works and dye-houses, where piece-goods are dyed blue, the vats are necessarily large, being generally about three feet wide by five feet long, and eight feet deep, made of iron, but sometimes of stone; and are sunk into the ground about half their depth. The goods to be dyed are stretched upon a frame, when the whole is lowered into the vat. Sometimes these frames are furnished with rollers, when, instead of fixing the piece on hooks, it is passed over these

rollers while in the vat, by which means long pieces are dyed perfectly regular in colour.

The vats for yarn or skein are small, being generally old wine or oil pipes; these are also sunk about half their depth into the ground. Wooden pins are put through the skein, and rest upon the edge of the vat, the skein is then turned over, the one half dipping in the liquor, the other half over the pins. The time of this operation varies according to the strength of the vat. The operation being continued some time, the skein is taken out, wrung, and exposed to the air, dipped again, and so on, alternately dipping and exposing, till the requisite shade is obtained.

To prepare the vat, it is filled to within a few inches of the mouth with water, the dyeing ingredients are then added—the proportions given in most chemical books, are 1 part (by weight) indigo, 2 parts sulphate of iron, and 3 parts lime; but this proportion of lime is too much; the practical dyer does not consider his vats in good condition when this proportion is used. The following proportions are considered proper for preparing one of these small vats—assuming all the ingredients good:—8 pounds of indigo, 14 pounds of copperas, and from 18 to 20 (not above 20) of lime. If the copperas be bad, a pound or even 2 pounds more of it may be required, along with 2 or 3 additional pounds of lime, to have the same results. These ingredients being put in, the whole is well stirred every two or three hours during the day, and, after settling for twelve hours, the vat is ready for use.

The chemical equivalents of lime may be calculated from the table of elements, and also the rate of combination. Thus, slaked lime is the hydrated oxide of calcium,—

Lime	Ca	= 20
	O	= 8
Water	H	= 1
	O	= 8
		37

And again we have—

Copperas	Fe	= 28
	SO_4	= 48
Water of crystallization	7 HO	= 63
		139

Thus, by equivalents, 37 lbs. of slaked lime should neutralize 139 lbs. of crystals of copperas; but as 77 gallons of water, at 60°, can dissolve only one pound of lime, it is easy to see how few pounds are required above the equivalent for copperas to form the lime solution of the vat to dissolve the indigogen. How it is that practice dictates such a quantity of lime to be used, is deserving of inquiry; we merely hint that it may be that the compound of indigogen and lime is more soluble than lime alone.

Woad and Pastel.—We have already alluded to these vegetables as yielding a variety of indigo, which has been long used for dyeing woollen goods. It is still extensively used for that purpose, especially on the continent; and as a description of the process, as it is there followed out, may be interesting to many of our readers, we extract the following from Dumas's Lectures on Dyeing, slightly altered from the translation, in the *Pharmaceutical Times*:—

"**Indigo Blue.**—We give a solid dye of indigo blue to wool by plunging it into an alkaline solution of indigo white, and then exposing it to contact with the air. The solution of indigo white is prepared in a vessel usually from eight to nine feet in depth, and six to seven feet in diameter. This size is very convenient for the requisite manipulations, and presents a large volume of water, which, when once heated, is capable of preserving a high temperature for a long time. This vessel should be made of wood or copper. It always bears the name of *vat*. These vats are covered with a wooden lid, divided into two or three equal segments. Over this lid are spread some thick blankets. Without this precaution the bath would come in contact with the atmospheric air; a portion of the indigo would absorb oxygen, and become precipitated. There would also be a great waste of heat.

"A most necessary operation, and one which has to be frequently repeated, consists in stirring up the deposit of vegetable and colouring matter which is formed in the vat, and intimately mixing it in the bath. For this purpose we employ a utensil called a *rake*, which is formed of a strong square piece of wood set on a long handle. The workman takes hold of this with both hands, and, dipping the flat surface into the deposit at the bottom of the vessel, he quickly

draws it up until it nearly reaches the surface, when, giving it a gentle shake, he discharges the matter again through the liquor of the bath. This manœuvre is repeated until the whole of the deposit seems to be removed from the bottom of the vessel. Before the tissue is dipped into the dye-bath, it should be soaked in a copper full of tepid water; it is then to be hung up and beaten with sticks. In this state it is plunged into the vat; it thus introduces less air into the bath, while it is more uniformly penetrated by the indigo solution. The cloth is now kept at a depth of from two to three feet below the surface of the liquid, by means of an open bag or piece of network fixed in the interior of an iron ring, which is suspended by cords, and fixed to the outside of the vat by means of two small iron hooks; the bag is thus drawn backwards and forwards without permitting it to come in contact with the air. When this operation has been continued for a sufficient length of time, the cloth is wrung and hung up to dry.

"Flock wool is also, for the purpose of dyeing, enclosed in a fine net, which prevents the least particle from escaping, and which is fixed in the bath in the same way as in the foregoing case.

"The many inconveniences attending the use of wooden baths, which necessitate the pouring of the liquor into a copper for the purpose of giving it the necessary degree of heat, have led to the general employment of copper vessels. These are fixed in brickwork, which extends half way up their surface, whilst a stove is so constructed at this elevation that the flame shall play around their upper part. By this means the bath is heated and kept at a favourable temperature without the liquor being obliged to be removed.

"The potash vats are usually formed of conical-shaped coppers, surrounded by a suitable furnace. These may be constructed with less depth, inasmuch as there is less precipitation induced in the liquor. By using steam for heating the vats, we might dispense with the employment of copper vessels, and so return to those of wood.

"The vats employed for dyeing wool are known under the names of the pastel vat, the woad vat, the potash vat, the tartar lee vat, and the german vat.

"The pastel is cultivated in France, Piedmont, England, and Saxony. It is distinguished into several varieties, ac-

cording to the localities in which it is grown. We have already stated that the pastel contains a blue-colouring matter, identical with indigo, and a fawn-coloured yellow matter, which may easily be separated by treating the pastel-balls by hot water, before the fermentative process is established. The woad is cultivated in Normandy; it contains less colouring matter, whether blue or yellow, than the pastel; its durability is also inferior to that of the last-named substance. M. Chevreul has given an analysis of the pastel, which will tend to throw some light upon its use.

"When the leaves are subjected to the action of the press, we obtain, on the one hand, a residue of a ligneous nature, and, on the other, a juice which holds in suspension sundry matters which give it a cloudy appearance. Thrown on a filter, it leaves a greenish matter or fecula, which is formed of chlorophylle, wax, indigo blue, and an azotized substance. The clear liquid, after passing through the filter, contains an azotized substance, coagulable by heat; an azotized substance, non-coagulable by heat; a red matter, resulting from the union of the blue-colouring principle with an acid; a yellow principle; gummy matter; some liquid sugar; a fixed organic acid; free acetic acid and acetate of ammonia; the oderous principle of the cruciferæ; a volatile principle, having the odour of osmazome; citrate of lime; sulphates of lime and potash; phosphates of lime; magnesia, iron, and manganese; nitre, and chloride of potassium.

"M. Chevreul has not discovered in these products any body possessed of the power of seizing upon oxygen in an energetic manner, and which would explain the action of the pastel in the indigo vat. Still we cannot doubt that the principles furnished by this matter intervene, to a certain extent, as combustibles, and that we must refer at least a part of their effect to this mode of action. The indigo should itself be selected with care. The Guatimala variety is preferred for the urinary or Indian vat, and the Bengal indigo for the pastel vat.

"**Pastel Vat.**—The first care of the dyer in preparing the vat should be to furnish the bath with matters capable of combining with the oxygen, whether directly or indirectly, and of giving hydrogen to the indigo. We must, however, be careful to employ those substances only which are incapable of

imparting to the bath a colour which might prove injurious to the indigo. These advantages are found in the pastel, the woad, and madder. This latter substance furnishes a violet tint when brought into contact with an alkali, and by the addition of indigo it yields a still deeper shade.

"In preparing the Indian vat we ordinarily employ one pound of fine madder to two pounds of indigo. The madder is here especially useful, by reason of the avidity of some of its principles for oxygen.

"The pastel vat, when prepared on a large scale, ordinarily contains from 18 to 22 lbs. of indigo; 11 lbs. of madder would suffice for this proportion, but we must also bear in mind the large quantity of water which we have to charge with oxidizable matters. I have invariably seen the best results from employing 22 lbs. to a vat of this size. Bran is apt to excite the lactic fermentation in the bath, and should, therefore, not be employed in too large a quantity: 7 to 9 lbs. will be found amply sufficient.

"The weld is rich in oxidizable principles; it turns sour, and passes into the putrid fermentation with facility. Some dyers use it very freely; but ordinarily we employ in this bath an equal quantity of it to that of the bran. Sometimes weld is not added at all.

"In most dye-houses the pastel is pounded before introducing it into the vat. Some practical men, however, maintain that this operation is injurious, and that it interferes with its durability. This is an opinion which deserves attention. The effect of the pastel, when reduced to a coarse powder, is more uniform; but this state of division must render its alterations more rapid. When the bath has undergone the necessary ebullition, the pastel should be introduced into the vat, the liquor decanted, and, at the same time, 7 or 8 lbs. of lime added, so as to form an alkaline ley, which shall hold the indigo in solution. Having well stirred the vat, it should be set aside for four hours, so that the little pellets shall have time to become thoroughly soaked, both inside and out, and thus be prepared for fermentation. Some thick coverings are to be spread over the vat, so as to preserve it from contact with the atmosphere. After this lapse of time, it is to be again stirred. The bath at this moment presents no decided character; it has the peculiar odour of the vege-

tables which it holds in digestion; its colour is of a yellowish-brown.

"Ordinarily, at the end of twenty-four hours, sometimes even after fifteen or sixteen, the fermentive process is well marked. The odour becomes ammoniacal, at the same time that it retains the peculiar smell of the pastel. The bath, hitherto of a brown colour, now assumes a decided yellowish-red tint. A blue froth, which results from the newly liberated indigo of the pastel, floats on the liquor as a thick scum, being composed of small blue bubbles, which are closely agglomerated together. A brilliant pellicle covers the bath, and beneath we may perceive some blue or almost black veins, owing to the indigo of the pastel which rises towards the surface. If the liquor be now agitated with a switch, the small quantity of indigo which is evolved floats to the top of the bath. On exposing a few drops of this mixture to the air, the golden yellow colour quickly disappears, and is replaced by the blue tint of the indigo. This phenomenon is due to the absorption of the oxygen of the air by the indigogen from the pastel; in this state we might even dye wool with it without any further addition of indigo; but the colours which it furnishes are devoid of brilliancy and vivacity of tone, at the same time that the bath becomes quickly exhausted.

"The signs above described announce, in a most indubitable manner, that fermentation is established, and that the vat has now the power of furnishing to the indigo the hydrogen which is required to render it soluble,—that contained in the pastel having been already taken up; this, then, is the proper moment for adding the indigo, which should be previously ground in a mill.

"We stated above that the liquor of the vat should be previously charged with a certain quantity of lime; we also find in it ammonia generated by the pastel; but a part of these alkalis become saturated by the carbonic acid gas along with the proper acids of the madder and of the weld, as well as by the lactic acid produced by the bran during fermentation. The ordinary guide of the dyer is the odour which, according to circumstances, becomes more or less ammoniacal. The vat is said to be either soft or harsh; if soft, a little more lime should be added to it. The fresh vat is always soft; it

exhales a feeble ammoniacal odour, accompanied with the peculiar smell of the pastel; we must, therefore, add lime to it along with the indigo; we usually employ from five to six pounds, and, after having stirred the vat, it is to be covered over. The indigo, being incapable of solution except by its combination with hydrogen, gives no sign of being dissolved until it has remained a certain time in the bath. We may remark that the hard indigoes, as those of Java, require at least eight or nine hours, whilst those of Bengal do not need more than six hours, for their solution. We should examine the vat again three hours after adding the indigo. We ordinarily remark that the odour is by this time weakened; we must now add a further quantity of lime, sometimes less, but generally about equal in amount to the first portion; it is then to be covered over again, and set aside for three hours.

"After this lapse of time the bath will be found covered with an abundant froth and a very marked copper-coloured pellicle; the veins which float upon its surface are larger and more marked than they were previously; the liquor becomes of a deep yellowish-red colour. On dipping the rake into the bath, and allowing the liquid to run off at the edge, its colour, if viewed against the light, is of a strongly-marked emerald-green, which gradually disappears, in proportion as the indigo absorbs oxygen, and leaves in its place a mere drop rendered opaque by the blue colour of the indigo. The odour of the vat at this instant is strongly ammoniacal; we also find in it the peculiar scent of the pastel. When we discover a marked character of this kind in the newly-formed vat, we may without fear plunge in the stuff intended to be dyed; but the tints given during the first working of the vat are never so brilliant as those subsequently formed; this is owing to the yellow-colouring matters of the pastel, which, aided by the heat, become fixed on the wool at the same time as the indigo, and thus give to it a greenish tint. This accident is common both with the pastel and the woad vats; it is, however, less marked in the latter.

"When the stuff or cloth has been immersed for an hour in the vat it should be withdrawn; it would, in fact, be useless to leave it there for a longer time, inasmuch as it could absorb no more of the colouring principle. It is, therefore, to be taken from the bath and hung up to dry, when the indigo, by

attracting oxygen, will become insoluble and acquire a blue colour. Then we may replunge the stuff in the vat, and the shade will immediately assume a deeper tint, owing to renewed absorption of indigo by the wool. By repeating these operations we succeed in giving very deep shades. We must not, however, imagine that the cloth seizes only on that portion of indigo contained in the liquor required to soak it. Far from such being the case, experience shows that, during its stay in the bath, it appropriates to itself, within certain limits, a gradually increasing quantity of indigo. We have here, then, an action of affinity, or, perhaps, a consequence of porosity on the part of the wool itself.

"**Woad Vat.**—These vats are extensively employed at Louviers, and in the manufactories of the north of France. The bath is prepared in the same manner as in the foregoing case: the finely-cut root is introduced into the copper along with 2 lbs. of pounded indigo, 9 lbs. of madder, and 15½ lbs. of slaked lime. The liquor is, after the necessary ebullition, poured upon the woad. This substance contains but a very small quantity of colouring principle; we must, therefore, add some indigo when preparing the vat, so as to indicate the precise instant when the mixture arrives at the point of fermentation so necessary for imparting hydrogen to the colouring principle, and for rendering it soluble. We must also use a larger quantity of lime, since the woad contains no ammonia resulting from previous decomposition, such as we find to be the case with the pastel of the south. When the vat is in a suitable state of fermentation, a rusty colour becomes manifest, in addition to the signs already described in speaking of the pastel vat; besides the ammoniacal odour, the bath always retains the peculiar smell of the woad. The pounded indigo is now added, and we proceed, in the manner already detailed, to reduce it to a state of solution fit for dyeing.

"The vats prepared by means of pastel have greater durability than those made with the woad; but it is thought that the colours given by the latter are more brilliant than those obtained from the former dye.

"**Modified Pastel Vat.**—This vat is about 7 feet in depth, and 6½ feet in diameter. It is made of copper, and heated by steam. The lid is composed of three segments, each of which

is formed of two planks, about an inch thick, and strongly secured together by bolts.

"The beating is performed in the usual way, with sticks, before the first dipping, after having moistened the cloth in tepid water. This operation is not subsequently repeated.

"This vat is prepared with 13 lbs. of indigo, 17½ lbs. of madder, 4½ lbs. of bran, 9 lbs. of lime, and 4½ lbs. of potash. Having filled the vat, we heat it to about 200° Fah., and, as soon as the water is tepid, introduce 441 lbs. of pastel. The liquor becomes of a yellowish-brown colour; small bubbles appear upon its surface, ordinarily at the end of four hours if the vat be heated by steam, but not until after eight or twelve hours where heat is applied by the common fire; in the latter case the mixture should be stirred every three hours. When the liquor displays the signs of fermentation, we add the above-mentioned ingredients, and cover the vat over; it is then to be set aside, stirring it every three hours, or oftener if the fermentative action be very rapid. Each time that it is stirred we are to add from 2 to 4 lbs. of lime; if fermentation proceed quickly we even use more, but in the contrary case less. After about eighteen hours we plunge into the vat three pieces of common cloth, measuring twenty to twenty-five ells in length each: when they have received six or seven turns they are to be taken out again. The object of this is to remove the excess of lime from the bath. The vat is then set aside for three hours, when it is to be stirred, and 13 lbs. of indigo, with 2 lbs. of madder, added to it. We now again apply heat to the mixture.

"If the vat contains a superabundance of lime, it will be unnecessary to add more: otherwise we throw in a further quantity. During the night it should be covered with a cloth, and a workman left to watch it. It is usually stirred once before the morning; but if it be deficient in lime, it will require this manipulation to be more frequently repeated, and also fresh lime added to it. On the following day the stirring should be continued every three hours, and so on for the next thirty hours, taking care to heat the vat from time to time. On the morning of the fourth day the dyeing may be commenced.

"The temperature should be maintained at a pretty uniform

point; if it be too hot the blue takes a red reflection, by reason of the madder contained in the liquid. A vat thus prepared will last three months; we may even work it for double that period, but after the third month it appears to lose some of its indigo.

"We maintain the power of the vat by introducing every night $2\frac{1}{4}$ lbs. of madder. Some indigo is also added twice or three times a-week. These additions are made in the evening. After the former, the vat is left at rest for forty-two hours; with the latter, only for twenty-four, at the same time observing the precautions already indicated. At the end of three months, or sooner, when we wish to stop the working of the vat, we exhaust the indigo; for this purpose we continue to charge it every night, for the space of a month, with madder, and dip into it white cloths, or more particularly woollen tissues, which become more or less loaded with the indigo. We must continue this plan until these matters take up no further colour. The dippings are to be performed twice a-day at first, but once only towards the termination. Many dyers make use of this bath for preparing a new vat; but it is better to throw this away and make it up afresh with common water.

"**Indian Vat.**—These vats are of more simple and of more ready construction than the pastel or woad vats. We are to boil in water a quantity of madder and of bran, proportioned to the weight of indigo which we wish to employ. After two hours' ebullition, we turn into this bath some tartar-lees, which are also to be boiled for an hour and a-half or two hours, so as to charge the bath with whatever soluble matter they may contain; after this ebullition, the bath should be allowed to cool, and the indigo, which has been previously ground, is then to be introduced. Supposing that we wish to employ 21 lbs. of indigo, the following would be the proportions used in preparing this vat:—41 lbs. of tartar-lees, 13 lbs. of madder, and 5 lbs. of bran. These vats are usually mounted in coppers of a conical shape; a small fire should be kept up around them, so as to maintain a moderate and uniform heat. The indigo will usually be found dissolved at the end of twenty-four hours, often even after twelve or fifteen hours. The liquor has a reddish colour in the new vats, and a green tint in those which are in a working state. The frothy surface,

as well as the brilliant-coloured pellicle, become manifested in this as in all other preparations of a like kind.

"This species of vat has to be renewed much more frequently than the woad and pastel vats, from the indigo being more difficult to dissolve, after a certain lapse of time. A moderate heat should be maintained in all these vats.

"**Potash Vat.**—This species of vat is extensively employed at Elbeuf for the dyeing of wool in the flock. It presents in all respects a perfect analogy with the Indian vat; in fact, the action of the tartar-lee, in the latter preparation, depends entirely on the carbonate of potash which it contains. The ingredients used in the preparation of the potash vat are—bran, madder, and the subcarbonate of potash of commerce.

"We obtain the deep shades in this species of vat with greater celerity than in all others, a fact which undoubtedly depends on the greater power which potash has of dissolving indigo than is possessed by lime. Experience proves that the potash vat has the advantage in point of celerity of nearly a third; but this is balanced by the inconvenience resulting from the darker shade, which we must attribute to the large quantity of colouring matter of the madder dissolved by the alkaline lee, and which becomes fixed on the stuff with the indigo.

"To render this vat in its most favourable state, the indigo should be made to undergo a commencement of hydrogenation, before turning it into the mixture; for this purpose we prepare, in a small copper, a bath analogous to that in the vat, to which the pounded indigo is added. This bath is maintained, for twenty-four hours, at a moderate heat, taking care to stir it from time to time. The indigo assumes a yellowish colour, becomes dissolved, and in this state is turned into the vat; we thus avoid many delays and losses in its preparation; and, indeed, it would be desirable if a similar plan were adopted with all these compounds.

"**German Vat.**—This vat is of nearly similar dimensions to that used for the woad, being three times the size of the potash vat. Its diameter is about $6\frac{1}{2}$ feet, and its depth $8\frac{1}{2}$ feet. Having filled the copper with water, we are to heat it to 200° Fah.; we then add 20 pailsful bran, 22 lbs. of carbonate of soda, 11 lbs. of indigo, and $5\frac{1}{2}$ lbs. of lime, thoroughly slaked, in powder. The mixture is to be well stirred, and then set aside

for two hours; the workman should continually watch the progress of the fermentation, moderating it more or less by means of lime or carbonate of soda, so as to render the vat in a working state at the end of twelve, fifteen, or, at the most, eighteen hours. The odour is the only criterion by which the workman is enabled to judge of the good state of the vat; he must, therefore, possess considerable tact and experience.

"In the process of dipping we introduce 84 lbs., 106 lbs., or even 130 lbs. of wool, in a net bag, similar to that used in the woad vat, taking care that the bag is not allowed to rest against the sides of the copper. When the wool has sufficiently imbibed the colour, we remove the bag containing it, and allow it to drain for a short time over the vessel. We operate in this way on two or three quantities in succession; we then remove the vat, and set it aside for two hours; we must be careful, from time to time, to replace the indigo absorbed by the wool, as also to add fresh quantities of bran, lime, and crystallized carbonate of soda, so as constantly to maintain the fermentation at a suitable point.

"The German vat differs, then, from the potash vat by the fact that the potash is replaced by crystallized carbonate of soda and caustic lime, which latter substance also gives to the carbonate of soda a caustic character. It presents a remarkable saving as compared to the potash vat; hence the frequency of its employment; but it requires great care, and is more difficult to manage. It also offers considerable economy of labour: one man is amply sufficient for each vat.

"The army cloth is usually dyed by means of the pastel vat, which gives the most advantageous results. We here make use of vats about $8\frac{1}{2}$ feet in depth, and 5 feet in diameter, into which we introduce from 361 lbs. to 405 lbs. of pastel or of woad, after previous maceration. The vat is to be filled with boiling water, and we then add to the bath 22 lbs. of madder, $17\frac{1}{2}$ lbs. of weld, and 13 lbs. of bran. The mixture is to be maintained in a state of ebullition for about half an hour; we next add a few pailsful of cold water, taking care, however, not to lower the temperature beyond 130° Fah.; during the whole of this time a workman, provided with a rake, keeps incessantly stirring the materials of the bath. The vat is then accurately closed by means of a wooden lid, and surrounded by blankets, so as to keep up the heat. It is now put aside

for six hours; after this time it is again stirred, by means of a rake, for the space of half an hour; and this operation should be repeated every three hours until the surface of the bath becomes marked with blue veins; we then add from six to eight pounds of slaked lime.

"The colour of the vat now borders on a blackish-blue. We immediately add the indigo in a quantity proportioned to the shade which we wish to obtain. The pastel in the foregoing mixture may last for several months; but we must renew the indigo in proportion as it becomes exhausted, at the same time adding both bran and madder. In general we employ—

"11 to 13 lbs. of good indigo for 100 lbs. of fine wool.

"9 to 11 lbs. of good indigo for 100 lbs. of common wool.

"9 to 11 lbs. of good indigo for 131 yards of cloth dyed in the piece.

"**Management of the Vats.**—A good condition of the vat is recognized by the following characters:—The tint of the bath is of a fine golden-yellow, and its surface is covered with a blueish froth and a copper-coloured pellicle. On dipping the rake into the bath, there escape bubbles of air, which should burst very slowly; when they vanish quickly, it becomes an indication that we must add more lime. The paste which is found at the bottom of the vat, green at the moment of its being drawn up, should become brown in the air; if, however, it remain green, this is a further sign that more lime is required. Lastly, the vat should exhale the odour of indigo. We usually complete the assurance of the vat being in a good state by plunging into it, after two hours' respite, a skein of wool, which, on being withdrawn after the lapse of half an hour, should present a green colour, but change directly to blue. We then once more mix the materials of the vat, and, two hours after, it may be considered ready for dyeing.

"These vats, like those already described, are provided with a large wooden ring, the interior of which is armed with a kind of network, for the purpose of preventing the objects which are intended to be dyed coming in contact with the materials at the bottom of the vat; we, moreover, take the precaution of enclosing the wool or cloth in bags. These tissues, when plunged into the bath, should remain there for

a longer or shorter time, according to the shade which we wish to obtain; one dipping, however, will never suffice for this object; usually we leave in the stuff for half an hour only; it is then to be taken from the bath, wrung, and exposed to the air. This operation is repeated until we have succeeded in procuring the desired shade; we ordinarily suffer three hours to elapse between each dipping. The heat of the vat should never be allowed to fall below 130° Fah. After each operation the bath must be well stirred, and fresh lime added; generally speaking, a pound a-day will suffice; we re-establish the indigo about every second day. When once this vat is well mounted, and we are careful to examine its working, we may dye from two to four batches a-day with it.

"When the stuffs have acquired the desired shade, they are first to be washed in common water, and then in a very weak solution of hydrochloric acid (about one part in a thousand;) after this they are again rinsed in pure water.

"The Indian vat is much more easily managed than the foregoing; it presents less danger of failure, from the fact that it is quickly exhausted, and also from the fermentative process, which is so difficult to govern in the pastel vat, here not having time to change in character. It is prepared by first introducing an equal quantity of madder and of bran, and a triple quantity of potash; this is to be gradually heated until it reaches a temperature of 167° Fah., and we then add to it the indigo, thoroughly agitating the matters for half an hour. The vat is maintained at a temperature of 86° to 100° Fah., by keeping it closely covered, and at the same time the mixture is to be stirred occasionally at intervals of twelve hours. It should by this time present a beautiful green shade, the liquor being surmounted by a copper-coloured pellicle and a purplish froth. We may now commence the dyeing, following the same course as with the pastel vat; but the stirrings being here repeated much more frequently than with the other mixture, we can dye a larger quantity of wool within a given time. When the vat ceases to give a brilliant blue, we must altogether renew it; if it be merely weakened, we add to it a small quantity of freshly-prepared liquor containing a few pounds of potash, and a little less bran and madder. In giving the dark and the clear sky-blues, we must be careful to employ a quantity of indigo proportioned to the colour which

we wish to obtain, or, better still, we may use the previously exhausted vat for the dark blue.

"When exposed to the influence of the putrid fermentation, indigo is decomposed and loses its colour. If rendered soluble, it obeys the impulse communicated to the azotized matters with which it is brought into contact, although, if macerated in pure water at the ordinary temperature, it is itself decomposed with great difficulty.

"The pastel and the woad are very prone to the putrid fermentation, by reason of the large quantity of azotized matters which they contain, as do all the cruciferæ; they require, therefore, considerable care in their employment.

"When a vat is mounted, if the fermentation be allowed to continue unchecked, after the appearance of the blue froth and the other signs already indicated, the liquor will acquire a yellow colour similar to that of beer; the froth will become white; it will give out a stale smell and lose its ammoniacal odour; after a few days it will turn whitish, and exhale a smell at first similar to that of putrified animal substances; then it will acquire the odour of rotten eggs, and set free sulphuretted hydrogen. The lime in the pastel and the woad vats, and the tartar-lee and potash in the other mixtures. are used for the purpose of preventing these accidents.

"Besides the oxygenated compound, which is formed by the combination of oxygen with the extractive matters of the plants held in digestion, there is a production of carbonic acid which saturates the alkaline lee, and forms a carbonate of lime in the pastel vat. We find this attached to the sides of the vat in such quantity, that the inside of these vessels becomes encrusted with it to a considerable depth. It is this product which dyers call the tartar of the vat; it effervesces with acids, and gives on analysis carbonic acid, lime, and a few particles of indigo. In the potash vat the solubility of the carbonate of potash prevents its deposition; but it is very probable that we have even here a formation of some carbonated products, perhaps in part formed at the expense of the carbonic acid of the air.

"The soluble extractive principle being the only matter which remains in solution in the bath with the indigo, the lime, &c., we have formed deposits which, varying both in their volume, and in the greater or less facility with which

they are precipitated during the various periods of fermentation, lead to a more or less considerable waste of time. If we plunge a piece of woollen tissue into a vat which has been recently stirred, it will acquire a dark colour, and will be found covered with brown stains which are with difficulty removed. When the woad or pastel vat has been stirred, it need be left two or three hours only before plunging in the stuff, at least during the early months of its working, inasmuch as the pastel, being but slightly divided and attenuated, is readily precipitated; but, when by reason of its extreme division, in consequence of repeated operations, it is thrown down with less facility, the dipping should not be performed oftener than three times in the day.

"The Indian vat requires less time than the others; we may even dye with it an hour after stirring the mixture. The potash, being soluble, forms no precipitate; while the ligneous fibre of the madder and the pellicles of the bran become deposited with great facility. We can also dip with these vats much oftener than with those made by pastel or woad."

Logwood.

Logwood is the *Bois de Campeche* and *Bois bleu* of the French, and the *Blauholz* of the German dyers. This wood is brought to us from Jamaica and from the eastern shores of the Bay of Campeachy; on this account it is distinguished in commerce by the names of *Campeachy* and *Jamaica* logwood. The former is considered much superior to the latter, and brings always a higher price in the market. Among botanists the logwood tree is known by the name of *Hæmatoxylon Campechiacum*. In a favourable soil it grows to a very great size; its bark is thin and smooth, but furnished with thorns: its leaves resemble the laurel; the wood is hard, compact, and capable of taking a fine polish; its specific gravity is much higher than water, in which it consequently sinks.

We are not aware who first introduced logwood as a dyeing agent; but its nature, and the art of using it as such, seem to have been but little understood in the reign of Queen Elizabeth; for we find her government issuing an enactment entirely forbidding its use. The document is curious, and

affords a good proof of the absurdity of a government interfering with the industry of its subjects. The act is entitled, "An Act for the abolishing of certeine deceitful stuffe used in dyeing of clothes;" and it goes on to state that, "Whereas there hath been brought from beyond the seas a certeine kind of stuffe called logwood, alias blockwood, wherewith divers dyers," &c., and "Whereas the clothes therewith dyed, are not only solde and uttered to the great deceyte of the Queene's loving subjects, but beyond the seas, to the great discredit and sclaunder of the dyers of this realme. For reformation whereof, be it enacted by the Queene our Soveraygne Ladie, that all such logwood, in whoes handes soever founde, shall be openly burned by authoritie of the maior."* This act was put forth in the 23d year of the Queen's reign, and was renewed again in the 39th, with the addition that the person so offending was liable to imprisonment and the pillory. Upwards of eighty years elapsed before the real virtues of this dyeing agent were acknowledged; and there is no dyewood we know now so universally used, and so universally useful.

Like many other valuable substances, logwood was long used before anything was known of the real nature of the colouring principle. Chevreul made a chemical examination of the wood, and found it to contain a distinct colouring substance, which he called hæmatine, a name which has since been changed to hæmatoxylin, to avoid any confusion with a substance having a similar name, contained in blood. Logwood contains, besides this colouring matter, resin and oil, acetic acid, and a double salt of potash and lime, with a vegetable acid. It sometimes contains also sulphate of lime, a little alumina, peroxide of iron, and oxide of manganese. These ingredients, however, vary; some woods having more than others, and others wanting some of them altogether. These varieties of constitution probably arise from the varying qualities of the soil on which the wood is grown.

We have frequently tried pieces of logwood as imported, and the average ash left after burning was 1·5 per cent., half of which was lime, with a trace of iron, and the remainder consisted of magnesia, alumina, and silica.

* Parke's Chemical Essays, 8vo., vol. i., page 632.

Chevreul's process for procuring the colouring matter is by subjecting logwood, after grinding, to digestion for a few hours in water at 120° or 130° Fah., afterwards filtering the liquor and evaporating to dryness; what remains is put into strong alcohol for a day; this is again filtered, and the clear liquor evaporated till it becomes thick; to this is added a little water, and evaporated anew; it is then left to itself, and the colouring matter crystallizes.

An improvement on this method has been recommended by Erdmann. The extract of logwood being evaporated to dryness, is pulverized, and mixed with a considerable quantity of pure silicious sand, to prevent the agglutination of the extract, and the whole allowed to stand several days with five or six times its volume of ether; the mixture being often shaken, the clear solution is poured off and distilled, until there is only a small syrupy residue. By this means most of the ether is saved; and this residue being mixed with a certain quantity of water, is allowed to stand for some days, when the hæmatoxylin crystallizes out, and may be dried between folds of blotting paper.

We are afraid both of these processes will be too tedious for adoption in a dye-house. We have seen some very good specimens of the hæmatoxylin obtained by evaporating a strong decoction of logwood nearly to dryness, and allowing it to stand for several days; a solid matter settles to the bottom, having a syrupy fluid above it; large crystals of hæmatoxylin appear to grow from the crust, giving it, when removed, a most beautiful velvety appearance. The crystals vary in length from one-fourth to five-eighths of an inch. They dissolve readily in hot water, but very slowly in cold; they are also soluble in alcohol. When dissolved in distilled water, the solution has a beautiful rich wine colour; but when the least trace of lime or iron is present in the water, (and very few waters are free of these,) its colour is materially altered. The action of re-agents is very powerful. Potash, when first put in, colours the solution violet; but this speedily passes into a purple, becoming brownish-yellow; and, in a little time, the mixture becomes almost colourless. The reason of this final change is, that a quantity of oxygen is absorbed; the hæmatoxylin is thereby destroyed, and the caustic alkali converted into a carbonate from the decomposition of the

colouring matter. Caustic soda has a similar effect; but the carbonate of soda is much more mild in its action than carbonate of potash.

An extract of logwood is sold in France in a crystalline form, and is obtained from a decoction of the wood. The crystals are dark red, nearly black; it is hæmatoxylin, with several impurities, but yields a very considerable quantity of colour.

The action of ammonia on hæmatoxylin is similar to that of potash and soda, but much more powerful in regard to its changing colour, and less destructive upon the substance. Some beautiful, and also amusing experiments may be performed with ammonia and the colouring matter of logwood. If a jar full of distilled water be taken, and a few drops of a solution of hæmatoxylin be added, not so much as to give a perceptible colouring to the water; on adding a few drops of ammonia, the water instantly takes a reddish tint, and changes so rapidly, that in two minutes, if the jar is large, the colour is so dark a violet shade, that the light can hardly be transmitted; in a little it becomes redder, and gradually passes away. This experiment may be repeated by placing the jar simply in the fumes of ammonia; the water begins to colour at the top, and as the absorption goes on, the colour passes gradually down, so that when it is dark at the top, it is slightly tinged at the bottom, and so on till the whole is converted into a dark violet, seemingly by magic.

Erdmann has been able to collect this compound of hæmatoxylin and ammonia, and finds that the colouring matter absorbs three equivalents of oxygen under the influence of the ammonia, and is converted into a substance which he names *hæmatein*. This hæmatein combines with ammonia, and forms a violet-black powder, which is soluble in water, giving it an intense purple colour, which spontaneously fades, and passes away by keeping.

The action of the alkalis upon logwood is similar to those described upon its colouring matter, and suggests the cause why those who add a little alkali to their logwood liquor while dyeing black, on purpose to give the colour of the logwood a richness, and prevent the action of the iron upon it, invariably have a bad grayish-black. Stale urine, indeed, which is most generally used for this purpose, if not used cautiously, pro-

duces the same bad colour from the ammonia which it contains. For this reason, also, we always wash from the lime, when it is used to pass the cloth through after being impregnated with iron, otherwise the lime on the cloth causes the colouring matter to undergo similar changes with the other alkaline substances, and gives the blacks thus dyed a grayish appearance. Indeed, so delicate is the action of all earthy and alkaline salts upon logwood, that it has been proposed as a test for the presence of lime in water.

In the chemical investigation of logwood, the colouring matter has been obtained in two conditions, differing in chemical composition only in one having more water than the other; but these researches have led to some curious and interesting speculations upon the relation which it has to other blue colouring matters of vegetables, particularly those of indigo and orceine, (the colouring matter of archil.) There is, however, this difference, that hæmatoxylin has no nitrogen, the others have; but instead of nitrogen it has water. Their comparative compositions are as follows:—

	C.	H.	O.	N.	Water.
Orceine	32	18	7	2	
Indigo blue	32	10	4	2	
Indigo white	32	10	2	2	2
Protohydrate hæmatoxylin	32	14	6	0	1
Perhydrate hæmatoxylin	32	14	6	0	3

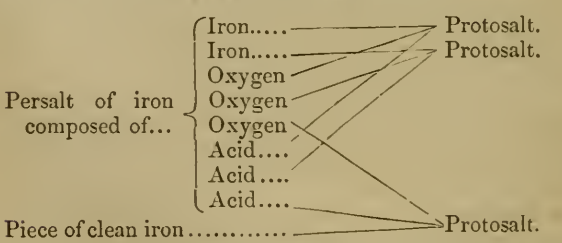
These analogies, in connection with the relations of colour, are striking; and if we could, by some transformation, obtain in the other two matters the permanence of indigo, the acquisition would be highly worthy of attention.

The action of metallic oxides upon the colouring matter of logwood is somewhat similar to the action of these oxides on logwood itself, varying considerably with the dissolving menstrua of the oxide, and the particular state of oxidization.

Protosalts of iron give Blue-black precipitates, permanent.
Persalts of iron .....Jet-black precipitates, which become brown.
Protosalts of tin.....Rich wine-colour precipitates, permanent.
Persalts of tin.....Deep wine-colour precipitates, which become brown.

Acetate of lead.....Brownish-black precipitate, which passes to gray.
Acetate of copper.....Greenish-black, passing to brown.
Salts of alumina.....Wine-colour precipitates, permanent.

These are the principal metallic salts used with logwood, and their effects. The acid in which the oxides are dissolved affects materially the results obtained; the iron is used in the state of sulphate or acetate; the tin as chloride, with free acid: lead and copper as acetates. The protosalts give, with log wood, the most brilliant, and also the most permanent colours: this should be constantly attended to. The iron protosalts, if exposed to the air, pass very readily into the state of persalts, especially if the salts be neutral—that is, have no more acid than is combined with the oxide. A little free acid prevents this change, but generally produces bad effects upon logwood. However, where the use of a protosalt of iron is necessary, any persalt in the mordant may be reduced to the proto-state by the immersion in it of a piece of clean iron, a few hours previous to using the solution. When an iron salt becomes peroxidized by exposure to the air, every third atom is precipitated as an insoluble oxide—the acid leaving this atom, and combining with two atoms iron, and three oxygen, to form a persalt, (page 154.) When a piece of iron is put into a persalt solution, the following reaction takes place:—



This operation ought to be performed just previous to using the solution, which should be as little exposed as possible; for when the salt is all converted into the proto-state, the atmosphere again speedily destroys it.

Decoctions of logwood are prepared in the dye-house either

by boiling or by *scalding;* if the logwood is chipped or cut, it requires to be boiled for two or three hours. This generally gives the purest and finest colours for *plumb tubs.* When the wood is ground, the decoctions are generally made by pouring boiling water upon it. Some dyers put the quantity required into a tub; fill this with boiling water; allow the grounds to settle, and decant the solution; but the best method is to use a basket, lined with cloth;—the logwood is put into the basket, and boiling water is poured upon it; the clean decoction filters through. No more logwood should be taken than what is to be used at the time, as it loses its dyeing properties by standing; the colour passes from a rich wine hue to a yellow-brown, and assumes a syrupy appearance; and colours dyed by it after this change takes place are always wanting in brilliancy: besides, it takes a greater quantity of stuff to produce the same depth of shade. This may be caused by a partial decomposition of the colouring matter, or of the other ingredients of the wood reacting upon the colouring matter.

Parkes, in his Chemical Essays, has the following observations bearing upon this subject:—"Considerable advantage is derived by the woollen dyers from the use of water in the preparation of rasped logwood. As the wood is cut into chips, they sprinkle it abundantly with water, and in that moistened state it is thrown into large heaps, and sometimes into bins of great size, where it is suffered to lie as long as is convenient. By this treatment the chips become heated, or they ferment, as the dyers call it, and thus undergo a very remarkable change; for, after having lain a few months in this state, they give out the colouring matter in the dyeing copper much more easily; and any given quantity of such chips will produce a more intense dye than could have been obtained from an equal quantity of chips which had not been thus heated. It is difficult to account for this, unless we suppose that the water becomes in part decomposed, and that its oxygen, uniting with the vegetable colouring matter, renders it more intense." We have found that, by damping the wood with boiling water a little before pouring the necessary quantity of boiling water upon it, the wood, in the language of the dyer, is much better *bled;* but we considered this to result from softening the particles of wood, and so making the colouring matter

more easily dissolved by the water afterwards applied. Whether anything more is effected by the practice noticed by Mr. Parkes, or if any decomposition takes place, we cannot say. If by fermentation is meant the formation of acids, we know that acids do not produce the effects stated; but if it is a fermentation caused by the decomposition of any substance having nitrogen as a constituent, the result would be the formation of ammonia, a substance, as we have already noticed, which has a powerful influence upon the colouring matter of logwood, and extracts it very rapidly—a property possessed, indeed, by all alkalis and alkaline earths. This is well known to dealers in logwood, who occasionally sprinkle it with water containing a little lime, which gives the wood a richness in colour, so that the poorest woods, thus *doctored*, appear equal to those of the finest quality. Such wood, however, never produces good light shades. The presence of an alkali may be detected in logwood, by taking a little in a tumbler, and allowing it to steep for a few hours in distilled water, and then trying the solution with delicate test-papers.

This practice of putting lime-water upon the ground logwood may be one reason why decoctions of ground logwood lose their colouring power so rapidly by standing; as all alkaline matters in connection with logwood, although they give, in the first place, a richness of colour, soon pass into a brown, and the colour decays.

There is yet no simple and accurate process for testing logwood which could be introduced to the dye-house, although there are few substances of apparently greater variety. The differences, however, often consist only in the moisture and in the *doctoring*.

The method generally adopted for judging of the value of logwood consists in comparing the colour of samples of yarn dyed by different specimens of it. A given weight of each of the logwood samples is macerated in boiling water, and then an equal quantity of mordanted cotton is dyed by each of the several decoctions: the depth and kind of colour produced are the test of the quality. With care this method is very satisfactory for practical purposes; but an oversight is often made in these trials in not taking the quantity of water which is in the sample. It is necessary that ground logwood should be a little damp, to prevent it flying away as dust, but it is also

requisite to avoid paying for the water put into it at the same rate as for logwood; care ought therefore to be taken not only to dry the samples, but also to ascertain the water contained in them. This will be rendered more apparent by stating the results of some experiments directed to this point. Samples of wood, as imported, before being ground or chipped, kept at a temperature of 212°, as long as it decreased in weight, gave a loss ranging from 9 to 16 per cent.: average 12 per cent. The moisture in ground logwood, as supplied to the dyer, ranges from 38 to 46 per cent.: average 42 per cent.; so that the amount of water added averages 30 per cent.

The moisture may be tried by putting a weighed sample of the ground wood upon a piece of paper, or on a plate for some hours in the drying-stove, when no wet goods are in it. In the experiments, of which the results are given above, we used a water-bath, which is preferable. Samples to be tried ought all to be previously submitted to the drying process.

Water is not the only thing added to logwood; a little lime is occasionally added to the water, which gives the logwood a bloom, and makes it appear better than it really is. In burning samples of ground logwood, and deducting the water that had been added, we have found the ash to vary from 2 to 2·3 per cent.

Were the usual mode of testing, by trying the depth of colour, to be applied with a doctored sample, and one not doctored, say half an ounce of each, the ground wood in each case put into a small basin, and filled with boiling water, and the decoction used to dye a skein of cotton, the doctored sample will be found to yield its colour immediately to boiling water, and the other slower—in which case, the former having yielded all its colour at once, may give a deeper dye than the other, and yet actually contain less colouring matter. The proper way of proceeding is to take 100 grains of each sample, put the whole quantity upon a filter, and pour boiling water upon it as long as the water passing through is coloured, then use all the liquor with cotton so mordanted as to take up all the colour. The remaining logwood thus exhausted should be nearly colourless; and by drying and weighing it, an approximation to the quantity of colour may be obtained. Good

logwood loses about 12·5 per cent. in this way after deducting all water.

We have already referred to the plumb tub and plumb spirits, and stated that if a salt of tin be put into a hot solution of logwood, there is a precipitate formed. If the neutral salt of tin be added to logwood, cold, there is a precipitate formed of a beautiful wine colour; but this precipitate is soluble in dilute muriatic acid—hence the reason why so much acid is used for the tin in the preparation of the plumb spirits.

The plumb tub is prepared as follows:—A decoction of logwood is made by boiling, continuing the ebullition until the specific gravity is 8° of Twaddell. This decoction is allowed to stand till it is perfectly cold; a quantity of tarry matter precipitates in the cooling, so that the clear liquor requires to be decanted. There is then added to it a quantity of *plumb spirits*, sufficient to raise the specific gravity to about 14° of Twaddell. After standing twenty-four hours, it is fit for use —which consists simply in immersing the goods for a short time, then taking them out and washing them. As this compound of tin and logwood is held in solution by the free acid of the spirits, whenever the cotton impregnated with it is put into water, the dye is rendered insoluble; the repeated washing is necessary to carry off all free acid. Occasionally in preparing the *plumb tub*, it happens from some cause, as want of care in making the spirits or the decoction, that the logwood gets all precipitated. This precipitate may all, or the greater part of it, be dissolved by adding hydrochloric acid; but then the tint of colour produced upon the goods will not be so blue: it will be more red, with a tendency to brown. Hydrochloric or nitric acid added to a cold solution of logwood, will make a plumb tub without tin; but there being no base, and the solution being soluble in water, it does not form a good dye, being nearly all removed by washing. But if the goods be previously prepared with a base, colours of various tints may be obtained by this means—which may be resorted to when a *plumb tub* is not at hand.

Brazil-Woods.

The *Bois de Pernambouc* of the French, and the *Brazilienholz* of the German dyers. There are several varieties of this wood, which are distinguished from each other by the name of the locality where they are obtained, such as Pernambuco, Japan, &c. In the dye-house they are often all named *peach-wood*, from an inferior sort often used, and obtained from Campeachy.

The Brazil-wood tree, called by botanists *Cæsalpinia crista*, is an American production, and, according to some authorities, gave the name to the country in which it grows,* *Brazil.* The Portuguese government discovered the value of the wood, and made it an object of royal monopoly; hence it came by the nearly forgotten name of *Queen-wood.* It grows mostly in dry places, and amongst rocks; its trunk is large, crooked, and full of knots.

The following paragraph upon these woods is taken from Bell's Geography:—"The *ibiripitanga*, or Brazil-wood, called in Pernambuco the *pao da rainha* (Queen's-wood,) on account of its being a government monopoly, is now rarely to be seen within many leagues of the coast, owing to the improvident manner in which it has been cut down by the government agents, without any regard being paid to the size of the tree or its cultivation. It is not a lofty tree. At a short distance from the ground, innumerable branches spring forth, and extend in every direction in a straggling, irregular, and unpleasing manner. The leaves are small and not luxuriant; the wood is very hard and heavy, takes a high polish, and sinks in water; the only valuable portion of it is the heart, as the outward coat of wood has not any peculiarity. The name of this wood is derived from *brasas*, a glowing fire or coal—its botanical name is *Cæsalpinia brasileto.* The leaves are pinnated; the flowers white and papilionaceous, growing in a pyramidal spike; one species has flowers variegated with red. The branches are slender, and full of small prickles. There are nine species."

The species *brasileto* is inferior to the *crista;* it grows in great abundance in the West Indies. The demand for this wood a few years ago was so great, owing to its being a little

* Southey's History of Brazil, vol. i.

cheaper than the other, that nearly the whole of the trees in the British possessions were cut down, and sent home—which Mr. Bell very justly terms improvidence. It is not now so much used, and is consequently scarcer in the market.

The wood known in commerce as *Pernambuco* is most esteemed, and has the greatest quantity of colouring matter. It is hard, has a yellow colour when newly cut, but turns red by exposure to the air. That kind termed *Lima-wood* is the same in quality. *Sapan-wood* grows in Japan, and in quality is next to the two named above. It is not plentiful, but is much valued in the dye-house for reds of a certain tint: it gives a very clear and superior colour. The quantity of ash that these two qualities of wood contain is worthy of remark. Lima-wood as imported gives the average of 2·7 per cent., while Sapan-wood gives only 1·5 per cent.: in both the prevailing earth is lime. The quantity of moisture in the wood averages about 10 per cent. That in the ground wood in the market about 20 per cent.

Peach-wood, or Nicaragua, and sometimes termed *Santa Martha-wood*, is inferior to the other two named, but is much used in the dye-house, and for many shades of red is preferred, although the colouring matter is not so great. It gives a bright dye. The means of testing the quality of these woods by the dyer is similar to that described for logwood, with the same recommendations and precautions.

The world is much indebted to the French chemists for their valuable researches into the colouring matters of the dye-woods. M. Chevreul long since obtained the colouring matter from Brazil-wood by the following process:—"Digest the raspings of the wood in water till all the colouring matter is dissolved, and evaporate the infusion to dryness, to get rid of a little acetic acid which it contains. Dissolve the residue in water, and agitate the solution with litharge, to get rid of a little fixed acid which it contains. Evaporate again to dryness, digest the residue in alcohol, filter and evaporate to drive off the alcohol. Dilute the residual matter with water, and add to the liquid a solution of glue, till all the tannin which it contains is thrown down; filter again and evaporate to dryness, and digest the residue in alcohol, which will leave undissolved any excess of glue which may have been added. This last alcoholic solution being evaporated to dryness, leaves

brezilin, the colouring matter of the wood, in a state of considerable purity."

Brezilin is very soluble both in water and alcohol, but from the hardness of the wood the colouring matter is not completely extracted except by boiling; even the method recommended for logwood does not dissolve all the brezilin. The decoction when boiled has a deep-red colour, but passes into a rich yellow-red by standing. Acids give this solution a yellowish colour, but render it unfit for dyeing operations. Alkalis communicate a violet colour which is very fugitive:—

Protosulphate of iron	Dark purple, not changed by standing.
Persulphate of iron	Blackish-brown, permanent.
Chloride of tin	Changes to a deep crimson.
Chloride of tin	With warmed liquor, a deep-red precipitate.
Acetate of copper	Dark purple.

Since these researches by Chevreul, M. Preisser has investigated these substances with great minuteness, and gives it as his opinion that the colouring matter of these, as well as of the other woods, are oxides of a colourless base. Thus brezilin is the oxide of a base which is without colour, and which he terms brezilein. Their compositions are—

	C.	H.	O.
Brezilein—Colourless base =	36	14	12
Brezilin—Coloured substance =	36	14	14

It will thus appear that the one is converted into the other by absorbing two proportions of oxygen, and that the reactions are allied to those of indigo and logwood already described.

The action of chromic acid, and of the chromates upon brezilin, is remarkable: they decompose each other, and produce a beautiful reddish-brown. The action of bichromate of potash with the decoction of Brazil-wood has been long taken advantage of in calico printing, and, by proper modifications, may also be applied in the dye-house. The remarks upon the pure colouring matter are applicable to the decoction of the wood; but the wood contains other mat-

ters, (small portions of astringent substance,) which are also soluble in the water, and which, accordingly, modify to a great extent the results produced by the combined action of the decoction and the pure colouring principle—a circumstance which should be constantly borne in mind by the dyer. It is known that decoctions of Brazil-wood improve by standing, often to the extent of giving a-half more effect as a dye; which is supposed to be owing to the oxidation and deposition of the tannin, and other foreign matters, injurious to the colour.

The nitrates of the metals almost all destroy the red colour of Brazil-wood, turning it into a dirty yellow. The salts of potash, soda, and ammonia, change the decoction into a rose colour, which soon passes away by standing. Alum throws down a bulky red precipitate. This substance, and the chloride of tin, are considered the proper mordants for Brazil-wood; but all the colours obtained by this wood are exceedingly fugitive, losing their brilliancy on a short exposure to air. The sun has a very powerful influence upon colours dyed by this wood. By a short exposure, the red colour assumes a blackish tint, passes into a brown, and fades away into a light-dun colour. These changes are supposed to be from the colouring matter being decomposed into water and some other volatile substance, leaving a part of the carbon free, which produces the black; heat is also very destructive to this colour; nevertheless, the consumption of this species of wood is very great, especially for dyeing what are termed fancy reds.

Santal or Sandal-Wood,

Commonly called *saunders-wood*, is a native of the East Indies. It differs from Brazil-wood in many of its properties; it is very hard, and gives but a weak decoction in water. The colouring matter of this wood is different from that of Brazil-wood: its composition is—

Carbon.	Hydrogen.	Oxygen.
16	8	32

and is termed *santaline*. It reacts with the salts of alumina, and gives red precipitates, which have more of a violet tint

than those of brezilin; but it does not react in the same manner with the chromates. Santaline is much more soluble in solutions of the astringent substances than in water; it is, therefore, boiled along with sumach, and is frequently used for woollens in dyeing browns and other mixed colours containing red. According to the investigations of the French chemists, this wood is a variety of barwood, at least the colouring matter is of the same composition.

Barwood.

This wood is brought principally from Sierra Leone. Its colouring matter has been examined by MM. Girardin and Preisser, who considered it the same as *santaline*. MacCulloch in his Commercial Dictionary makes a distinction between barwood and camwood; but they are found to be the same in chemical composition, only coming from two different places.

The following is MM. Girardin and Preisser's description of this wood:—

"This wood, in the state of a coarse powder, is of a bright-red colour, without any odour or smell. It imparts scarcely any colour to the saliva.

"Cold water, in contact with this powder, only acquires a fawn tint after five days' maceration; 100 parts of water only dissolve 2·21 of substances consisting of 0·85 colouring matter and of 1·36 saline compounds. Boiling water becomes more strongly coloured of a reddish-yellow, but on cooling it deposits a part of the colouring principle in the form of a red powder. 100 parts of water at 212° dissolve 8·86 of substances consisting of 7·24 colouring principle and 1·62 salts, especially sulphates and chlorides. On macerating the powder in strong alcohol, the liquid almost immediately acquires a very dark vinous-red colour. To remove the whole of the colour from fifteen grains of this powder, it was necessary to treat it several times with boiling alcohol. The alcoholic liquid contained 0·23 of colouring principle and 0·004 salt; barwood contains, therefore, 23 per cent. of red colouring matter, whilst saunders-wood, according to Pelletier, only contains 16·75.

"The alcoholic solution behaves in the following manner towards re-agents:—

Distilled water, added in great quantity	Produces a considerable yellow opalescence. The precipitate is re-dissolved by the fixed alkalis, and the liquor acquires a dark vinous colour.
Fixed alkalis	Turn it dark crimson or dark violet.
Lime-water	Ditto.
Sulphuric acid	Darkens the colour to a cochineal red.
Sulphuretted hydrogen	Acts like water.
Salt of tin	Blood-red precipitate.
Chloride of tin	Brick-red precipitate.
Acetate of lead	Dark violet gelatinous precipitate.
Salts of the protoxide of iron	Very abundant violet precipitates.
Copper salts	Violet-brown gelatinous precipitates.
Chloride of mercury	An abundant precipitate of a brick-red colour.
Nitrate of bismuth	Gives a light and brilliant crimson red.
Sulphate of zinc	Bright red flocculent precipitate.
Tartar-emetic	Abundant precipitate of a dark cherry colour.
Neutral salts of potash	Act like pure water.
Water of barytes	Dark violet-brown precipitate.
Gelatine	Brownish-yellow ochreous precipitate.
Chlorine	Brings back the liquor to a light yellow, with a slight yellowish-brown precipitate, resembling hydrated peroxide of iron.

"Pyroxylic spirit acts on barwood like alcohol, and the strongly-coloured solution behaves similarly towards re-agents. Hydrated ether almost immediately acquires an orange-red tint, rather paler than that with alcohol. It dissolves 19·47 per cent. colouring principle. Ammonia, potash, and soda, in contact with powdered barwood, assume an extremely dark violet-red colour. These solutions, neutralized with hydrochloric acid, deposit the colouring matter in the form of a dark reddish-brown powder. Acetic acid becomes of a dark-red colour, as with saunders-wood."

The difficulty of its slight solubility in water is overcome by a very ingenious arrangement. The colouring matter, while hot, combines easily with the proto-compounds of tin, forming an insoluble rich red colour; the goods to be dyed are impregnated with protochloride of tin combined with sumach; the proper proportion of barwood for the colour wanted is put into a boiler with water and brought to boil; the goods thus impregnated are put into this boiling water containing the rasped wood, and the small portion of colouring matter dissolved in the water is immediately taken up by the goods. The water thus exhausted dissolves a new portion of colouring matter, which is again taken up by the goods, and so on, till the tin upon the cloth has become, if we may so term it, saturated; the colour is then at its brightest and richest phase.

A good deal of attention and skill is necessary to know the exact point to take the goods out of the bath, otherwise the dyer may either have the colour poor, or by being in too long, give it a brown colour. It is not, therefore, every dyer who can dye good barwood red.

In dyeing with this wood it must be in contact with the goods: the particles of the wood must mix with the fibre. To have the wood in a bag, even, does not answer; and therefore great care is necessary in putting the mordanted goods into the dyeing bath, that there be no loose mordant upon them; for if there is, the wood (being in the bath) will take up this mordant and become dyed, and so retain a corresponding portion of the colouring matter, and to that extent cause loss. Inattention to this precaution is, moreover, frequently the cause of great irregularity in the shades; and even with the greatest care, the *wood-grounds* come out of the bath richly dyed. Barwood is not used along with other matters

for compound colours, in the same way as the other red woods are for dyeing cotton; but it is occasionally so used in dyeing woollens. The dyer has no means of testing the value of this dyewood, owing to its insolubility in water. In a piece of wood as imported, we found moisture 11 per cent. and only 0·5 per cent. of ash. In ground samples the moisture ranges about 20 per cent. and the ash 1·2. The colouring matter is very soluble in dilute ammonia. By passing ammonia water through a weighed quantity upon a filter, until all soluble matters are dissolved out, then drying the residue, the average of good barwoods gives—

Wood remains	73·4
Water at 212°	18·2
Colouring matter	8·4
	100·0

By neutralizing the ammonia the colour is precipitated as a lake.

It is recommended in some works upon dyeing as a general rule, that as all colours that are dyed in boilers begin to take on the dye when the solution is lukewarm, the goods should be put in at that heat, and kept in till boiling. This may be best in the case of woollen, and even with some colours, such as barwood and madder, upon cotton; but it is not good as a rule for cotton. Generally, indeed, the quicker cotton is dyed the better, and when there is a mixture of colouring matters used, long working causes that colour, which has the greatest attraction for the mordant, to prevail at the expense of the others, even although the attraction when the goods were newly put into the mixture may have been simultaneously equal and mutual.

Camwood

Is another species of red wood sometimes used in the dyehouse, imported from Sierra Leone. The colour obtained from it is more permanent, and in many instances much more beautiful than those termed Brazil-woods. The precipitates from a decoction of the wood are more yellow than those

afforded by the Brazil-woods—which explains why the colours dyed by it have a certain degree of richness not obtained with the other woods. It is not so easily affected by alkaline substances, and appears to contain more tannin than the Brazil-woods. With it—

Protosulphate of iron.....Gives a brownish-black precipitate.
Persulphate.....A reddish-brown.
Protosalts of tin.....Give the solution a very bright carmine-red colour, but little precipitate.
Lead salts.....A rich orange precipitate after standing some time.
Acetate of copper.....A light reddish-brown.
Nitrate of silver.....A reddish-yellow precipitate.
Perchloride of mercury....Light orange by standing.
Alum.....Gives the solution a beautiful red colour.

This wood may also be used for browns and other composition colours where Brazil-wood is commonly used; it is more soluble in water, has other advantageous properties, and may be used as a substitute for many other purposes in which the best Brazil-woods are employed.

Fustic or Yellow-Wood.

This dyestuff has been long known. It is uncertain when it was introduced as a dye-drug, but mention is made of it in a book published in 1692. The botanical name of the tree which produces this drug is *Morus tinctoria*. It grows spontaneously in Brazil, and in several of the West Indian islands, where it attains to a great height. The wood is of a sulphur colour, with orange veins, and contains two colouring matters; the one resinous, and not soluble in water; the other very soluble in this menstruum, producing a deep-yellow colour, having a light orange cast. This substance has been long used for dyeing yellow, is still extensively employed for producing that colour upon woollen and silk, and is the principal

ingredient in dyeing greens upon these substances; but it is seldom used for cotton.

The colouring matter of this wood has been studied by M. Chevreul, who has given it the name of *morin*. If we take one pound of ground fustic and boil it for a short time in a gallon of distilled water, and then pass the solution rapidly through a filter, to separate the woody particles; as the solution cools it becomes turbid, and a quantity of the colouring matter is precipitated. If allowed to stand for several days, a goodly quantity of morin may be obtained in a crystalline form. Every practical dyer who has used fustic, knows that if his decoction of this wood stand over, it loses its colouring properties, and that therefore it should be used immediately after boiling. The yellow decoction of this wood gives with the following re-agents:—

Alkalis..... An orange colour with a green tint.
Protochloride of tin...A reddish-yellow.
Perchloride of tin.....A rich yellow.
Alum.....A canary yellow.
Acetate of lead.....An orange-yellow, but dirty.
Acetate of copper.....A brown tint.
Protosalts of iron.....A greenish-olive tint, which darkens by standing.
Persalts of iron.....The same.
Sulphuric acid .....A red precipitate by standing.
Nitric acid.....A red precipitate.

The morin precipitated from the solution, is soluble in water with difficulty, but dissolves freely in a weak alkali, from which it may be precipitated. The colouring matter is often found crystallized in veins of the wood. The base of this colouring substance is also considered to exist in the white state; but it passes into yellow by absorbing oxygen.

This dyewood was partially superseded for the dyeing of yellows upon cotton by quercitron bark, and both are now almost totally displaced by bichromate of potash and lead. There are still, however, some greens dyed by fustic upon cotton yarn. The yarn is first dyed blue by the blue vat, and then passed through a little pyrolignite of alumina; it is next

wrought in a hot decoction of fustic, which communicates a beautiful rich shade of green.

Light cotton fabrics, as gauzes and muslins, are also occasionally dyed green by fustic. For this purpose the wood is used in the same manner as the quercitron bark. Fustic is also used with other woods for compound shades, as drabs, fawns, olives, &c., and is much used with logwood in dyeing black, as well on cotton as upon silks and woollens.

Young Fustic,

Called also *Venetian Sumach*, was long used in France under the name of *fustet*, for giving a yellow dye. These names caused a good deal of confusion, which is to some extent obviated by the prefix *young* to this wood, the yellow-wood being *old* fustic. Young fustic is a shrub (*rhus cotinus*) which grows principally in Italy and the south of France, where it is cultivated for the purposes of dyeing. When cut down it is stripped of its bark, and broken into small pieces, in which state it is met with in commerce. This wood contains a large quantity of yellow-colouring matter named *fusteric*. It is soluble in water, and in that state gives the following reactions with other substances: namely, with—

Tin salts.....An orange-yellow precipitate.
Iron salts.....An olive-green colour.
Acetate of lead.....A yellowish-white.
Alkalis in solution....Change the colour to red.

This colouring matter has a strong attraction for oxygen, a property which affects its use as a dye. The colours being fugitive, it is seldom used alone as a dye, but as an assistant to strike some particular tint. It is not used in cotton dyeing.

Bark or Quercitron

Is the inner bark of a tree (the *quercus nigra* of botanists) which grows spontaneously in North America. Its dyeing properties were first made known to the public by Dr.

Bancroft, in 1784, and were very soon appreciated. Two years after he obtained an act of parliament, vesting in him the exclusive use and application of it for a certain term of years.

A decoction of quercitron bark has a yellow-orange colour. If the decoction be made very strong, it deposits a portion of the colouring matter in cooling. It contains a great quantity of tannin, which is always dissolved in the decoction, and which gives the solution of bark a greater variety of uses. A decoction of the bark gives the following reactions with other matters :—

Alkalis	Deepen the colour of the solution.
Lime	A precipitate of a yellowish-red colour.
Protchloride of tin	A yellowish-red precipitate.
Alum	A slight precipitate cold, but more when hot.
Acetate of alumina	A bulky reddish-yellow precipitate.
Acetate of lead	A reddish-yellow precipitate.
Acetate of copper	A greenish-yellow precipitate.
Salts of iron	Dark olive-green precipitates, passing into brown.
Hydrochloric acid and nitric acid	Reddish-yellow precipitates.

The pure colouring matter of bark has been extracted and investigated by Chevreul and Bolley. It is termed *quercitrine*, is a crystalline substance of a sulphur-yellow colour, and like the other extractive colouring matters, is considered to be the oxide of a colourless base. The composition of quercitrine is given as follows :—

Carbon.	Hydrogen.	Oxygen.	Water.
16	8	9	1

A decoction of bark standing until it becomes stale, loses much of its dyeing properties. The yellow matter is deposited, and what remains in solution is of a darker hue, and gives a dull colour when used for dyeing.

Bark was extensively used in the dye-house for many years for the purpose of dyeing yellow, and almost completely superseded the use of fustic, both from its beauty and also its

cheapness; but its use for that purpose has been superseded by the bichromate of potash. Its principal use now in the cotton dye-house is to form the ground for certain browns, and for dyeing green upon light muslin cloth; but catechu has now nearly superseded it for browns. The quantity of tannin combined with it makes it very useful for olives; goods impregnated with iron, and passed through a decoction of bark, take a beautiful olive. When used for dyeing green, the mordant employed is acetate of alumina; but for yellow, which is now only dyed upon yarn for particular purposes, the mordant used is chloride of tin (spirits).

When bark is used for brown upon yarns, it is done thus: —The goods are dyed a deep yellow by being steeped in sumach, and then passed through the spirits, out of which they are wrought in a boiling decoction of bark, *raised* with spirits; that is, having a quantity of spirits put into the bark solution. The goods are washed from this, and afterwards passed through a mixture of logwood and Brazil-wood, according to the shade of brown required. And we would here draw attention to a very interesting fact, observed first by Mr. Thom of Manchester, namely, that amongst the colouring matters and bases there is an elective affinity, which if not studied, will lead to several errors. We quote on this subject from "Parnell's Applied Chemistry:"—

"But the combinations of alumina, &c., with soluble colouring matters seem to be cases of true chemical combination, taking place in definite proportions, and under the influence of different degrees of attractive force for different colouring principles. Thus, alumina has a stronger attraction for the colouring principle of madder than for that of logwood, and a stronger attraction for that of logwood than for that of quercitron. When a piece of cloth impregnated with alumina is immersed in a decoction of quercitron bark, it acquires a fast yellow colour; if the same cloth is washed for some time and kept in a hot decoction of logwood, the alumina parts with the colouring principle of quercitron to combine with that of logwood, and the colour of the cloth becomes changed from yellow to purple. If the same cloth is next immersed for a few hours in a hot infusion of madder, the alumina parts with the colouring principle of logwood to unite with that of madder, the colour of the cloth changing from purple to red.

The quantity of alumina on the cloth does not appear to diminish while these substitutions are taking place. These interesting facts were communicated to me by Mr. John Thom of the Mayfield print works."

Now the same law is applicable when the mordant is tin; so that a quantity of goods being dyed yellow as described, and then put into a hot solution of logwood, a quantity of the yellow is displaced by the colouring matters of the logwood and Brazil-wood. Every dyer knows when he has browns of a deep shade, how difficult it is to bring them up, should he fail to strike the proper tint at the first dip; if he is necessitated to continue working in the logwood and Brazil-wood, he is very apt to run his colour poor in yellow by dissolving it off; and to remedy this evil he next adds fustic or bark, with very questionable success. We have often experienced these difficulties when dyeing browns by the process described above, with an aluminous mordant upon the cloth instead of tin.

Flavine.

Within these few years a vegetable extract bearing this name has been introduced into the art. It is brought from America in the state of an impalpably fine powder, very light, and of a dun colour It is used in the dye-house as a substitute for quercitron bark, to which, for some purposes, it is superior. The mode of preparing it, is by dissolving it in hot water, with which it gives a sort of turbid solution. It should be used when newly dissolved; for if allowed to stand, it deposits a brownish-yellow mass, in consequence of its not being all completely soluble in water. If boiled in distilled water until all the soluble matter is taken up, and the clear solution decanted, it soon yields a deposit. The colour produced by flavine is never good until raised. A colour dyed by it weakens gradually when a little sulphuric acid has been added; but what remains retains its brilliancy by raising, and in respect of this property it differs from bark.

The quantity of colouring matter in flavine is very great: its value as compared with bark is as 16 to 1, or one ounce

flavine is equal to one pound of bark. A portion burned left 4·4 per cent. of ash; and a solution of it gives the following reactions with salts:—

Persalts of iron .....Olive-black precipitates.
Protosalts of iron.....Deep greenish-black precipitates.
Protosalts of tin .....Lemon-yellow precipitates.
Persalts of tin.....Orange-yellow precipitates.
Alumina.....A rich yellow precipitate.
Acids lighten the colour of the solution, and alkalis deepen it, rendering it redder.

Weld or Wold.

This vegetable is extensively cultivated in France, and many other parts of Europe, for the purposes of dyeing yellow. It is found in commerce in small dried bundles. The more slender the stem is, the better is it considered for dyeing. Both the seeds and the stems are used, as they both contain the colouring matter; but the seeds are considered to contain it in greatest quantity. The colouring matter approaches very nearly to that of quercitron in chemical properties; and of all the vegetable dyes, it is least acted upon by acids and alkalis; which gives to the dye, so far as these substances are concerned, great permanence. But it has this counteracting disadvantage, that the colour rapidly fades or passes away when exposed to the action of air and light; it then becomes oxidized, and in consequence has been abandoned for almost all purposes where bark can be used. It is still, however, occasionally used as a yellow dye for silks and woollens; and also for some mixed colours. A decoction from weld is made in the same way as that of most other vegetable dyes; the wood, whether in bunches or chipped, is merely put into a boiler with water and boiled. Sometimes the bunches are put into a bag of coarse cloth. This decoction is of a yellow colour with a reddish tint, and has a bitter taste and a peculiar odour:—

Alkalis.....Change it to a brighter yellow.
Acids.....Darken the yellow.
Alum.....A yellow precipitate.
Protochloride of tin..A yellow precipitate.
Acetate of lead.....A yellow precipitate.
Sulphate of iron.....A yellowish-olive precipitate.

The colouring matter of this dye has been obtained in needle-shaped crystals by sublimation, and is then termed *lutéoleine.* We have referred to a use to which weld is applied in the making up of pastel and woad vats, (page 313.) The weld was long used as a dye for woollen and silk before it was used for cotton; its introduction as a dye for this substance is connected with a clever fraud. "In the year 1773, the sum of £2,000 was granted by act of parliament to a Dr. Williams, as a reward for his discovery of a fast green and yellow dye upon cotton yarn and thread. This supposed fast dye was given by the combination of weld with a certain mordant, the composition of which the patentee was permitted to conceal, that foreigners might not enjoy the benefit of his discovery, while he on his part engaged to supply the cotton and thread dyers with his dye at a certain fixed price. The mordant used was supposed by chemists to be a solution of tin alone, or of tin and bismuth, which gives to weld yellow the power of resisting the action of acids and of boiling soapsuds; although it is not proof against the continued action of the sun and air. This defect, however, was not easily discernible, in consequence of the ingenious method which, according to Dr. Bancroft, the inventor employed to obtain a favourable testimony of the dyers upon the subject. He caused his specimens of dyed yarn to be woven into pocket-handkerchiefs, and gave them to be worn in the pockets of those who were afterwards to attest to the goodness of his dye, and as handkerchiefs worn in pockets were not exposed to the action of the sun and air, this want of permanence was not discovered until some time after the reward had been paid for an invention which proved of little or no value."

Turmeric.

This is another substance formerly used in dyeing. It is principally brought from the East Indies and from China. It is the roots of a plant named *curcuma langa*, and resembling ginger; it is reduced to powder, and in this state is met with in the market. The colouring matter is extracted by boiling in water; and decoctions of it have a peculiar smell and bitter taste. The colour is very fugitive, fading rapidly in the air; and there is no proper mordant for it. We have occasionally seen it used for giving a peculiar tint to greens and light browns; but this only could serve for a short time. The colouring principle of this vegetable has also been extracted, and is known in chemistry under the name of *curcumine*. A decoction of turmeric, or paper dyed with it and kept from exposure, is much used in testing for the presence of alkalis, which give to the dye a red-brown colour.

Persian Berries.

These berries are the root of the *rhamnus tinctoria*, a plant growing in the Levant and south of France, &c. They yield a bright-yellow colour, used by artists and occasionally by dyers; but the dye is very fugitive. There are two kinds of Persian berries; one large, plump, and clear in colour, the other small, wrinkled, and brown. The colouring matter of each kind has also certain distinctive properties, caused, it is believed, by the one being in full maturity, the other unripe. The large and mature berries are the best, giving a greater quantity of dye, and of superior quality of colour. The colouring matters extracted from the two varieties are named *chryso-rhamnine* and *xantho-rhamnine*. These have some interesting reactions with bichromate of potash, and other oxidizing agents.

Safflower or Carthamus.

This is an annual plant, cultivated in Spain, Egypt, and the Levant. There are two varieties of it, one having large leaves, and the other smaller ones; the last is the best.

It is only the flower of this plant that is used for dyeing. When the flowers are gathered, they are squeezed between two stones to express their juice: they are afterwards washed with spring water; next taken in small quantities and pressed between the hands and laid out upon mats to dry. These cakes are covered up during the day to prevent the sun from shining upon them—which would not only destroy the colour, but dry the cakes too much, and thereby cause further deterioration. They are kept exposed to the dews of night, and turned over occasionally, till dried to the proper point, when they are packed up for the market. It is in this state they are procured by the dyer.

Safflower contains two colouring substances. The one is yellow, very soluble in water, and of no use to the dyer. To free the safflower from this yellow-colouring substance is a particular part in the manipulation of this dyestuff. The other colouring substance is red, and is extracted from the vegetable after the yellow substance has been washed away, by means of alkaline carbonates. This substance is used very extensively for dyeing the various shades of pinks, crimsons, roses, &c., upon silk, and also for the same colours upon cotton, with lavender, lilac, pearl-white. The mode of preparing safflower for the purpose of extracting the red matter from it, was for a long time that recommended by Berthollet, and followed by all other writers upon the subject; namely, putting a quantity into a fine bag, "tramping" it with the feet in water until the yellow colour was dissolved and washed away; the mass left was then treated with an alkali to extract the red matter. But although this red-colouring matter is insoluble in water, it will be found that the bag in which it is tramped becomes a deep crimson-red, which can only be produced by its imbibing this red matter. It proceeds, we think, from a very fine powder, probably *carthamine*, adhering to the stuff like the pollen of the flower, and which floats away in the water. It is much heavier than the ordinary carthamine, and collects as a sediment at the bottom of the vessels used to hold the safflower; but when tramped in bags, this powder is expressed and imbibed by the bag, which becomes strongly dyed, thereby causing a loss of the dye. To avoid this, the safflower is now put into a tub without any bag, with as much water as will cause the whole to float freely. A very little

tramping or agitation is sufficient to reduce the cakes to a soft flocculent mass, which is the sole use of tramping. It is next removed to a cask or tub, provided with a false bottom, covered with fine haircloth. In the lower or true bottom, is a plug-tap. This vessel is filled with clean water, which is let out by the plug at the bottom; it is filled again, and so on, until the water passing through is not coloured yellow. After this, there is put into it a measured quantity of pure water—about three gallons to the pound of safflower—in which is dissolved a little carbonate of soda, or carbonate of potash, (pearlash does well,) about an ounce to the pound of safflower. Some kinds require less than others; but care ought to be taken that too much is not used, as it destroys the brightness of the colour. This, being dissolved in water, is put into the tub containing the safflower, well stirred, and allowed to stand for about seven hours; the plug is then taken out, and the clear liquor drawn into a proper vessel. This liquor contains the red dye which has been extracted by the alkali. The remaining safflower is afterwards washed by pouring upon it a little more water made slightly alkaline, and allowed to steep a short time; but if fine light colours are to be dyed directly from the solution, this second extract does not answer so well, as the shade is not so pure. This second extract is commonly kept and used instead of clear water for the next parcel of safflower; or if it is wanted for this purpose, a little acid is added to the liquor, and a piece of old cotton is allowed to steep in it until it has extracted all colouring matter, and which is afterwards recovered for use, as will presently be described.

The liquor extracted from the safflower contains both red and yellow-colouring matter. For this reason silk goods are not dyed directly by this extract, as the silk takes up a portion of the yellow, which renders the colour more of a brick hue than is due to the rose and pink. To dye silks, any old cotton yarn is dyed first by the safflower extract; the cotton takes up nothing except the red. This cotton is then thoroughly washed in cold water till the water coming from it is perfectly clear; it is then steeped for a little in water made slightly alkaline by carbonate of soda or potash, which extracts the red from the cotton, and forms the dyeing solution for silk. The silk to be dyed pink, generally receives a *bottom* or *ground* by passing it through a weak solution of cudbear

or archil, so as to form a flesh or light lavender colour—the depth being regulated according to the shade of pink wanted. It is then put through the safflower solution, which must previously be rendered acid by a little lemon-juice, vinegar, or sulphuric acid. When the safflower liquor is exhausted, the silk is washed in cold water, and finished by passing through a little water made acid by lemon-juice or tartar; neither vinegar nor sulphuric acid should be used in the finishing process.

To dye cotton pink, the liquor is used as extracted from the vegetable; the goods require no previous preparation, except to be well bleached. The quantity of liquor used varies according to the shade required; one pound of safflower to the pound of cotton gives a dark rose; and the other shades in proportion, according to the tint required.

The goods are first wrought in the alkaline solution for five or six minutes and then taken out, and vitriol added to the solution until it tastes decidedly sour; the goods are again immersed and kept working in this till the solution is perfectly exhausted. The ascertaining of this point requires a little experience, as exhaustion is known by the operator holding a little between him and the light; when, if there is no tinge of red, the solution is spent. The goods are now to be well washed by passing them through three or four tubsful of clear cold water; they are then finished by passing them through a little water, with just sufficient tartar to make the liquid taste sour.

It must be borne in mind that, in dyeing with safflower, the water ought to be pure and always cold; a very little heat destroys the beauty of the colour; the goods ought also to be dried cold, and preserved carefully from sunshine. The colours obtained by safflower are the prettiest that can be had upon cotton, but they are fugitive.

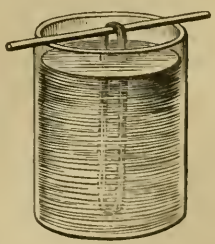
The most beautiful lilacs, puces, and lavenders, are obtained by safflower and prussian blue; but it is one of the most difficult colours to produce of equal shade. The goods are generally first dyed a blue by nitrate of iron and prussiate of potash, (see page 160,) and then put through the safflower solution, previously made acid; but the rapidity with which the cloth takes up the red, renders it almost impossible to get a perfectly even dye. Another method is to dye the cloth in the first instance pink, and then to dye it blue. This method

gives a more equal dye, but it is liable to serious objections. The nitrate of iron used acts upon the colouring matter, oxidizing and destroying its beauty and depth, thus causing loss, and making this colour exceedingly expensive. Persulphate of iron may be used instead of the nitrate, as it is not so corrosive, and will preserve the tint of the safflower much better.

We mentioned in our introductory remarks that one essential condition in all dye-drugs, before they could be used as such, was that they should be in solution; but carthamus is an exception to this rule: when it is in a soluble state, it is not a dye, and must be rendered insoluble before it will act as such. Although the cotton is generally passed through the alkaline solution before acid is added, still this will not produce the dye, but merely secures an equalized colour under the rapid action with which the fibres imbibe the solid colouring matter after acid is applied.

This fact favours the opinion that the cotton imbibes the colouring matters in the same way as they are imbibed by charcoal—the fibres of the cotton, like those of silk and wool, being hollow.

This action is not merely a capillary attraction, such as shown with glass tubes. When very small glass tubes are placed with their ends dipping into a solution, the fluid is observed to rise in them to a great height inversely as the hollow diameters of the tubes, and then remain stationary; but if such tubes are placed in a vessel containing the carthamus in suspension, although they become filled with the liquor they do not exhaust the liquor of the suspended colouring matter; whereas the fibres of the cotton, placed into this fluid, extract all the colouring matter from the water, and become literally filled with it. Thus, if we take a vessel filled with water, having in it carthamus rendered insoluble by an acid, and suspend a skein of cotton in it for a few hours, the cotton will absorb the whole colouring matter, and leave the solution clear—indicating thereby a distinct power of attraction exercised between the fibre and colouring particles, and also a circulation of the



fluid through the fibre or tubes of the cotton, which, indeed, is true, more or less, of any solid substance so finely divided as the carthamus, and diffused in water along with fibres of cotton. In the case of precipitates, the more dense they are the smaller is the quantity of solid matter imbibed by the fibre.

When a little safflower solution has an acid put into it, and is allowed to stand for a time, the red carthamine precipitates as a fine red lake, and is sold as such adhering to saucers for dyeing ribbons, &c. An extract of safflower has also been recently introduced into the market for the use of dyers, but we have, as yet, had too little experience of its use to speak of it with confidence.

Although safflower colours may be the most simple and easily dyed of all others, still, from their delicate reactions with other matters, there are few substances subject to so much risk of being destroyed. If the water is not pure they will dry brown. A little acetic acid, cream of tartar, or tartaric acid, is generally added to the last water from which they are finished to preserve the tint; but too much or too little of these will produce perceptible effects upon the shades. Great care has to be taken in the drying: it should be done in a perfectly dry stove, not hot, and having ample space between each parcel, as a very little steam produces a yellow surface. The goods are generally dried in the cold; but care is necessary that no sun-rays touch them; also that they are not injured by steam or smoke entering the sheds where they are drying. If all necessary precautions are not taken, the dyer has the mortification, as well as expense, of putting the goods through at least the last acid solution, and if they are much touched, he is obliged to re-dye them.

The view that carthamine, or the red-colouring matter of safflower, is the oxide of a colourless base, as in the case of the woods we have referred to, has been objected to by many investigators, whose experiments and reasoning bear evidence of care and judgment; thus adding an interest to the subject of vegetable colouring matters, and showing the practical man that there is yet before him much to be discovered, and that a careful observation of all the reactions and circumstances connected with his operations will stand a fair chance of being rewarded with success.

Madder.

This vegetable rivals indigo as a dye-drug, both from the beauty and permanence of the colours it produces, and also from the variety of shades which it is capable of furnishing by the combinations of its colouring matters. It is the root of a plant or shrub called *rubia tinctorium*, cultivated in the Levant, and in several western countries of Europe, especially in France and Holland. The East Indies also furnish a quantity of it, and within these few years a large importation has taken place of a species termed *rubia memsgista*, which contains much more colouring matter than the best madders of Europe. Its culture has been often attempted in England, but without success. In the Levant the madder is collected only once in five years; but in France it is gathered every three years. It is only the root of the plant that is used for dyeing. In removing the root from the ground, it is carefully cleaned, and, when the season is favourable, it is spread out in the air to dry. French madder is generally more imperfectly dried than that from the Levant, and consequently contains more water of vegetation, and to that extent it is comparatively less valuable. It is sometimes dried in a stove, to allow it to pulverize. The dryness of the article is judged of by the fracture when a piece of the root is broken transversely by bending it.

When the roots are perfectly dry, if they are broken or cut with a knife, they present to the eye a reddish-yellow colour, which passes to a dense brownish-red when the piece is moistened; but the more yellow the root appears when dry, the more colouring matter does it yield. Madder, when fresh, and after being cut or ground to powder, (in which state it is generally used by the dyer,) has a heavy sweet smell, with a somewhat earthy flavour. The product of grinding is generally of three kinds. The first is formed of the epidermis, or skin of the roots, and comes off in fine filaments by slight pressure. This is collected separately, and forms what is termed the *mull*—which is of very inferior quality. The second consists of the annular portion of the root; and the third of the ligneous or centre portion; but generally these two qualities are mixed.

The varieties of madder in commerce are distinguished by

the name of the country from whence they are brought, and by the appearance they receive in the preparatory process through which they pass previous to their reception at the dye-house.

Levant Madder is in the form of shoots or fibres, of greater or less length, and very slender; brown externally, and pale orange-red internally. It is merely cleaned of earth and dried, and is imported from Smyrna, Cyprus, &c.

Dutch Madder is ground, but so very coarsely as to enable the buyer to judge of the nature of the root from which it is prepared. It has a greasy feel, and a strong nauseous odour. Its colour varies from a brown to an orange-red; the brown is inferior. It becomes damp when exposed to the air, a property which can be taken advantage of to judge of its quality: if a little of it is exposed in a damp place, when good, its colour passes from the brownish-orange tint to a deep red.

The madder of Holland is said to be *cropped* or *uncropped*, according as the barky matter of the root is separated or not, from the ligneous part in the process of pounding through which it passes. This madder is never employed fresh, but is kept at least a year, and it is better to be kept three years before it is used. It may be kept several years longer without being impaired. During the first years it is kept it undergoes some internal change, and becomes much brighter in colour; the powder adheres together, forming a mass very difficult to remove from the cask, and swells so, that the bottom of the cask often assumes a convex form. If kept for too long a time it becomes deteriorated: the portion in contact with the cask loses its brilliancy, and becomes brown, and this change gradually extends through the whole mass. After this change has taken place, it is unfit for dyeing fine reds or light tints, and can be used only for dark colours.

The marks of Dutch madder are—

Mull O.....		Mull.
Superfine.....	or	Fine pulverized.
Cropped or uncropped		Superfine pulverized.

Alcase Madder.—This madder is met with in commerce in a state very similiar to that of Dutch madder; but although the operation of cropping is generally performed upon it, that term is not used in designating it. It readily absorbs mois-

ture from the air, and also acquires a deep-red tint when exposed in a damp atmosphere, as that of a cellar. Like Dutch madder, it is not employed fresh: it is in its best condition when about two years kept, but it deteriorates much sooner by keeping, and also agglomerates into a mass, and swells. It is inferior to the madder of Holland; its odour is more penetrating, and its taste less *sweet*, but with an equal degree of *bitter;* its colour is more yellow, passing into brown, with much less of the orange tint. A little experience in comparing the two sorts soon enables the dyer to distinguish the one sort from the other.

Madder of Avignon.—This madder is deservedly much esteemed. There are several varieties of it, some due merely to the modes of preparation, and others to the soil on which the plant grows. It is ground into a fine powder, which feels dry to the touch, and does not absorb moisture so readily as the other kinds of madder; but when exposed to a humid atmosphere, it also undergoes a change. Its odour is very agreeable; the taste a mixed sweet and bitter, the last predominating; and its colour varies from a pink or rose hue to a deep red, or reddish-brown. The best qualities are obtained from those roots which grow in marshy or swampy ground, and places enriched by admixture of animal or vegetable matters. The roots from such a soil are generally of a deep-red colour, while those from less favourable grounds are of a rose or pink tint. It is by mixing these kinds in different proportions that the variety of madders from this locality are obtained. The several qualities have various marks, besides the ordinary marks, as—

P. to signify.....*Palus*, (marshy.)
R. — .....Roseate.
P. P. — .....Pure *palus*, (marshy.)
R. P. P. — .....Purest red *palus*, (marshy.)

The actual commercial marks, according to the order of their quality, are—

S. F. for *superfine*—containing all the matter of the root.
S. F. F. for *fine superfine*—containing all the ligneous matter of the root, the mull or bark, or outside portion being separated.

E. S. F. F. for extra fine fine—containing the heart or centre of the root, and the internal part of the oily ring which surrounds it; being also twice sifted so as to separate completely from the mull, &c.

These three varieties may themselves vary according to the nature of the roots, and the manner in which they are dried, and otherwise prepared; but it is from these that all the various mixtures are made; and the tact of the manufacturers consists in mixing them so as to produce the qualities required by the consumer.

Avignon madder can be used fresh, although it is better to be kept for twelve months. It does not cake or agglomerate in the cask, but when kept too long it becomes deteriorated in quality, undergoing the same kind of decomposition as the other madders.

Madder is often adulterated by mixing with it brick-dust, red or yellow ochres, sand, and clay, or by adding sawdust of certain woods, as mahogany, logwood, sandal-wood, &c. &c. The mineral adulterations may be detected by putting some of the suspected madder in a large glass vessel, and adding to it a quantity of pure water: the madder floats, and the mineral adulterations sink to the bottom. We thus readily obtain an approximate idea of the quantity of adulterating matters present, and by carefully removing the floating madder, and then filtering the liquor, the mineral substances may be separated and weighed. We may also proceed by burning a small portion of the madder and seeing the ash that remains; we have in this way tried various samples, having $8\frac{1}{2}$ per cent. of ash.

When the adulterants consist of sawdust or other ground vegetable matters, their detection is much more difficult; indeed, the only means likely to be at all successful, is to weigh a portion of the suspected madder, and to try its colouring powers by a piece of prepared cotton: except where chemical skill can be applied, the colouring matter of the madder can be extracted, and compared with other known qualities.

Some of the French dyers use a *colorimeter* for judging of the quality of their madder. It depends upon a principle similar to that of Mr. Crum's chlorimeter for testing the

strength of bleaching powder, (see page 81.) A weighed quantity of madder, of known quality, is boiled, and the decoction is put into a glass vessel; similar quantities of the madders to be tried are treated in the same manner, and placed in a glass vessel of similar size and form, and the tint of colour is judged by comparison. Of course, the test solution may be diluted by a measured quantity of water, and by using a graduated glass, their comparative values, estimated by the rate of dilution, &c., may be easily ascertained. But this method is subject to many errors, as when any adulteration has been practised on the madder, by addition of other vegetable colouring matters, such as sapan-wood, &c.

Madder has been the subject of a great many chemical investigations, the study of which is highly useful to those who use this dye-drug in their operations.* The first investigation into the chemical properties of madder led to the discovery of two distinct colouring matters—one yellow, which is very soluble in cold water, and named *xanthin;* the other red, moderately soluble in hot water, is called *alizarin.* Several methods of extracting alizarin by sulphuric acid have been proposed, but the following is probably the most simple in practice:—"One pound weight of madder is mixed up with an equal weight of concentrated sulphuric acid, the vessel so closed up that no heat is evolved, and allowed to stand in a cool place for three or four days: by this process all the constituents of the madder are converted into charcoal, except the alizarin. When this charring process is completed, the mixture is carefully dried, and then digested in alcohol, which dissolves the alizarin and leaves the charcoal. The solution may now be diluted with water, and put into a retort, and kept at a heat of 170° Fah.: the beak of the retort being connected to a receiver, the alcohol distils over, and is recovered. Water and alizarin remain in the retort, which being poured out and filtered, the alizarin remains upon the filter in a state of great purity. It is of a beautiful red colour, and gives the same colour to boiling water.

Alizarin is soluble in turpentine, naphtha, and fat oils; chlorine turns it into a yellow-brown; sulphuric acid dis-

* See 2d, 5th, and 6th vols. Chemical Gazette; 1st vol. of Pharmaceutical Times; 33d vol. Phil. Magazine, &c.; Thomson's Vegetable Chemistry.

solves it, and, at the same time, enlivens the colour; muriatic and nitric acids both dissolve it, changing the colour from red to yellow.

Alkalis.....A violet colour.
Alumina.....A deep red-brown precipitate.
Oxides of tin .....Precipitates of the same appearance.

Phosphates have a very powerful attraction for alizarin, so much so, that when animals take any madder into their system, the bones, which contain a considerable quantity of phosphates, become coloured red. This fact is well known to dyers who are in the habit of using madder in their operations, and necessarily often tasting it. When taken in quantity, the urine is coloured by it.

From the above reactions of alizarin with other substances, it was supposed that it constituted the true colouring of madder; and means were soon adopted to separate this colouring matter from the vegetable, and use it pure; but it was afterwards found that a fixed dye could not be obtained by pure alizarin, and therefore it did not constitute all that was required in giving the dye. This led to further investigations, productive of further discoveries respecting these colouring matters. It finally appeared that madder has five different colouring matters, which have been named—

Madder purple, | Madder orange,
Madder red, | Madder yellow,
Madder brown;

each of which may be obtained by the following operations:—

Madder Purple.—The madder is washed in water at about summer heat, then boiled in a strong solution of alum for an hour; the clear liquor is afterwards decanted, and sulphuric acid added, which precipitates the madder purple along with a number of impurities. These are removed by washing with boiling water, then with pure muriatic acid, and afterwards dissolving in alcohol. Madder purple is soluble in hot water; and if pure it gives the water a dark-pink colour. If the water contains lime, a great part of the colouring matter is precipitated as a reddish-brown substance. Cotton, saturated with the acetate of alumina, is dyed a bright red, provided

the quantity of madder purple be not too great for the aluminous base, but if so, the colour will have more of a purple tint. A boiling solution of alum forms with the madder purple a cherry-red solution; caustic potash forms with it a fine yellowish-red colour; the carbonate of potash and soda have a similar effect; and sulphuric acid produces a bright red or rose colour.

Madder Red is separated from madder purple in consequence of its not being soluble in a strong solution of alum. It is obtained by boiling madder in a weak solution of alum, by which a reddish-brown precipitate is obtained. This precipitate is repeated, and boiled in pure muriatic acid, then washed carefully with water and boiled in alcohol. This dissolves both madder red and madder purple; but by gently evaporating the alcoholic solution until it is very much concentrated, and then allowing it to cool, an orange-coloured precipitate is formed, which is collected and repeatedly boiled in a *strong* solution of alum, as long as the alum solution comes off coloured: the insoluble portion is madder red. It is a yellowish-brown powder, and imparts to cotton, impregnated with acetate of alumina, a dark-red colour, when in excess; but if the mordanted cotton be in excess, a brick-red colour is produced. Caustic potash gives a violet, carbonate of soda a red, and sulphuric acid a brick-red solution.

Madder Orange is distinguished from the two former colours by its slight solubility in alcohol. It is prepared by macerating madder for twenty-four hours in distilled water, the infusion being strained off and allowed to repose a few hours. The liquor is carefully decanted and filtered through a paper filter, upon which the madder orange remains. It may be washed with cold water, and afterwards purified by spirits of wine, in which it is not soluble. It is a yellow powder, soluble in boiling water, and imparts to cotton impregnated with an aluminous mordant a bright-orange colour, when in excess. A boiling solution of alum forms with madder orange a yellow solution; caustic potash gives a dark rose, carbonate of soda an orange, and sulphuric acid an orange-yellow colour.

Madder Yellow is characterised by its great solubility in water. It is a yellow gummy mass; communicates to mordanted cotton a pale-nankeen colour, but does not of itself

form a true dye. Madder which contains much of this ingredient is of inferior quality, as the yellow becomes so incorporated with the other colours, as materially to deteriorate them, and to require several operations to free the goods from it afterwards.

Madder Brown is a brownish-black dry mass, obtained in the preparation of the other colouring matters. It is neither soluble in water nor alcohol, is of no importance as a dye-drug, and does not enter into any of the colours dyed by madder.

Madder Acids.—Besides these five colouring matters, madder contains two acid substances, named *madderic* and *rubiacic* acids. They have no known dyeing properties, and are only mentioned here to show the intimate knowledge which chemists possess of this agent; indeed, so important were any investigations in madder considered, that the *Societe Industrielle de Mulhouse* for several years offered 2,000 francs as a premium for the best analytical investigation of this substance.

Useful Products.—It will be observed in this brief outline of the colouring matters of madder, that only three of them are of importance to the dyer, viz., the *red*, *purple*, and *orange*. It will also be observed that these three colouring substances have a similarity of action towards mordanted cottons. Taken singly, not one of them forms a good dye; but they constitute the elements which together produce the richest and most permanent reds which the modern dyer possesses. Indeed, practically it is only necessary to consider madder as containing no more than two colouring matters, as was formerly supposed, viz.,—the dun or yellow, which constitutes the impurity of the madder, and which the dyer endeavours to get rid of, and the red-colouring matter. The former, or yellow, does not combine with the cloth alone, and probably not at all, but it has a strong affinity for the other colouring matters, and combines with them when they are upon the cloth, and has to be separated from them by after processes. The latter, or red, which is a combination of all the three, the red, the purple, and the orange, unites with the cotton as one, and is known to the dyer only in the aggregate state. This colouring matter is difficultly soluble in water, and therefore no strong decoction of it can be obtained by boiling, so that it is not very applicable for compound

colours, and therefore of little avail in the *fancy* dye-house. Many extensive fancy dyers, indeed, do not consider madder as even belonging to their province. They use it very seldom, except to give a peculiar tint to some light compound colours, and for fast salmon colours, pinks, &c. When deep colours are to be dyed by madder, the goods must be put into the dye-bath or boiler along with the madder, in a way nearly similar to that described for barwood.

Madder in the hands of the skilful operator can be made to produce a vast variety of colours and tints, by corresponding changes of his mordants, and the colours are all characterised by a degree of permanency which no other vegetable dye-wood produces. The operations, however, are generally much more tedious than those for ordinary fancy colours; and much skill is also required in preparing and applying the proper mordants for madder colours, and also in the preparation of the cloths for the different mordants.

Madder Preparations.—There are two colouring substances prepared from madder, which are now being much used in dyeing and calico printing, and which seem to embrace all those different colouring principles we have been describing; these are *garancine* and *colorine*. The former was first formed and described by MM. Robiquet and Colin, as far back as 1828; but it was long before it was introduced generally to the trade. Garancine is a chocolate-coloured powder, having no taste or smell; but from differences in the modes of preparation, and also in the qualities of the madders from which it is prepared, it varies very much in quality, which is probably the reason why it has been repeatedly taken up and abandoned by dyers. Ultimately, however, means of testing its quality, &c. were devised, and have proved favourable to its more constant employment. The manner of forming garancine, as given by MM. Robiquet and Colin, is to take one part of madder, and five or six parts of cold water, and allow the mixture to macerate till the following day; the whole is then thrown upon a cloth-filter, and when drained is subjected to pressure. It is then to be steeped again in cold water and pressed, and so on for the third time. When these operations are completed, almost half as much sulphuric acid (by weight) as there was of the madder in its first state, is to be diluted with water, so as to raise the temperature as much as possible, and

this is added to the pressed madder while hot, and stirred as rapidly as possible; the temperature is then raised and kept at 212° for about an hour. A quantity of water is then added, and the whole is thrown upon a filter; water is poured over the residue until it passes through the filter without taste of acid, and the matter collected is then pressed and dried, and passed through a sieve. This constitutes garancine. The sulphuric acid used is not altered in character, but seems only to have carbonized some of the impurities in the roots, without affecting the red-colouring matter. There are several other methods of preparing this substance, but not differing essentially from that described; as throwing the rough madder into water, and heating it to the boiling point, then adding the sulphuric acid, after which the whole is filtered, washed and dried, and reduced to powder, &c. During these few years the consumpt, and consequently the manufacture of garancine, has greatly increased. The mode of testing garancine is similar to that described for madders; either by the depth of dye produced on mordanted cotton, or by means of the colorimeter. In 1843 a patent was taken for extracting garancine from the waste madders of the dye-house, and we believe has been productive of great saving and advantage. The substance of the process thus patented is:—

"The invention consists in manufacturing a certain colouring matter called garancine from refuse madder, or madder which has been previously used in dyeing, such madder having ordinarily been thrown away as spent and of no value, and the said colouring matter called garancine having been produced heretofore from fresh or unused madder. A large filter is constructed outside the building in which the dye-vessels are situated, formed by sinking a hole in the ground, and lining it at the bottom and sides with bricks without any mortar to unite them. A quantity of stones or gravel is placed upon the bricks, and over the stones or gravel common wrappering, such as is used for sacks. Below the bricks is a drain to take off the water which passes through the filter. In a tub adjoining the filter is kept a quantity of dilute sulphuric acid, of about the specific gravity of 105, water being 100. Hydrochloric acid will answer the several purposes, but sulphuric acid is preferred as more economical. A channel is made from the dye-vessels to the filter.

The madder which has been employed in dyeing is run from the dye-vessels to the filter; and while it is so running, such a portion of the dilute sulphuric acid is run in and mixed with it as changes the colour of the solution and the undissolved madder to an orange tint or hue. This acid precipitates the colouring matter which is held in solution, and prevents the undissolved madder from fermenting or otherwise decomposing. When the water has drained from the madder through the filter, the residuum is taken from off the filter and put into bags. The bags are then placed in a hydraulic press to have as much water as possible expressed from their contents. In order to break the lumps which have been formed by compression, the madder or residuum is passed through a sieve. To 5 cwt. of madder in this state, placed in a wood or lead cistern, 1 cwt. of sulphuric acid of commerce is sprinked on the madder through a lead vessel similar in form to the ordinary watering-can used by gardeners. An instrument like a garden spade or rake is next used, to work the madder about so as to mix it intimately with the acid. In this stage the madder is placed upon a perforated lead plate, which is fixed about five or six inches above the bottom of the vessel. Between this plate and the bottom of the vessel is introduced a current of steam by a pipe, so that it passes through the perforated plate and the madder which is upon it. During this process, which occupies from one to two hours, a substance is produced of a dark-brown colour approaching to black. This substance is garancine and insoluble carbonized matter. When cool, it is placed upon a filter and washed with clear cold water until the water passes from it without an acid taste. It is then put into bags and pressed with a hydraulic press. The substance is dried in a stove and ground to a fine powder under ordinary madder stones, and afterwards passed through a sieve. In order to neutralize any acid that may remain, from 4 to 5 lbs. of dry carbonate of soda for every hundredweight of this substance is added and intimately mixed. The garancine in this state is ready for use."—Sealed August 8, 1843.

The following is the action of garancine when put into different qualities of water and with re-agents:—

Distilled water, *cold*.....A pale yellow in about 24 hours.
Distilled water, *boiling*...A pale reddish-yellow tint.
Spring water, *cold*.....Less coloured than with cold distilled water.
Boiling spring water.....Less coloured than with boiling distilled water.
Cold lime water.....Paler than with either cold distilled or spring water.
Water with a little sulphuric acid.....Greenish-yellow tint after some hours.
Water with H Cl .....The same, but darker in tint.
Water with NO_5 .....Still darker tint, passing into a brownish-blue.
Water with acetic acid...Faintly yellow.
Strong acetic acid.....Acquires a beautiful reddish-yellow colour.
Ammonia.....Becomes red immediately, and after a few hours so deep as not to be transparent.
Water with ammonia.....Beautiful red colour.
A solution of caustic soda.....Dark red-brown.
Water with carbonate of soda.....Bright reddish colour.
Cold alum water.....Chrome-red colour.
Boiling alum water.....A dark-red colour.

The mordants used for dyeing with garancine are the same as for dyeing with madder. It only yields its colour to the mordanted cloth at a boiling temperature, and the water of the bath or boiler does not become coloured. A little sumach is often used along with the garancine for reds.

If the water used in dyeing be a calcareous spring, a little sulphuric acid, just enough to give the water a sour taste, should be added, but when sumach is used, the acid is not required. The dye obtained by garancine is generally more brilliant and lively than from madder. In printing the colour is not so liable to run upon the white, and the goods are consequently more easily cleared than when madder is used.

Colorine is the residue left by distilling the alcoholic tincture made by treating garancine with spirits of wine. It is

considered to be impure alizarine. When this product is taken from the retort, it is in the form of an extract; but diluted with water, separated, subjected to pressure, and then dried and pulverized, it resembles yellow ochre. It leaves a deep stain on the fingers if moistened by it. It is prepared in France at a cheap rate, and used in calico printing by being dissolved in ammonia, thickened with gum, and applied to the cloth previously mordanted.

The mordants used for madder and the colouring preparations obtained from it, are the acetate of alumina, acetate of iron, and mixtures of these; the chlorides of tin, acetate of lead, and acetate of copper, and sometimes ammoniuret of copper. The last two are often used as alterants. In using iron mordants it is of the utmost consequence that they be the protosalts; hence iron liquor is more frequently used than sulphate of iron, which salt is more apt to become peroxidized.

In dyeing with madder there are many operations not practised in the fancy dye-house, such as dunging, &c.

Munjeet

Has been tried as a substitute for madder. It contains more colouring matter, and is found in commerce in bundles consisting generally of thick and thin stalks; the thin stalked variety contains less colouring matter than the thick, and has the bark on; whereas the thick stalks are barked. The stalks of the munjeet are very dry, light, and porous; the fracture exhibits a congeries of empty tubes. The powdered munjeet is composed of the thin and thick stalks mixed.

Reds dyed with munjeet are very brilliant, but fugitive, being destroyed by a short exposure to light and air. This vegetable cannot, therefore, be a proper substitute for madder.

Annotta, or Arnotto.

This substance, the *Roucou* of the French dyers, is obtained from a shrub originally a native of South America, and now cultivated in Guiana, St. Domingo, and the East

Indies. It is termed the annotta tree, or *bixa orellana*, and seldom exceeds twelve feet in height. The leaves are divided by fibres of a reddish-brown colour, and are four inches long, broad at the base, and tending to a sharp point. The stem has likewise fibres, which in Jamaica are converted into serviceable ropes.

"The tree produces oblong bristled pods, somewhat resembling those of a chesnut. These are at first of a beautiful rose colour, but, as they ripen, change to a dark-brown, and bursting open, display a splendid crimson farina or pulp, in which are contained from thirty to forty seeds, somewhat resembling raisin stones. As soon as they arrive at maturity these pods are gathered, divested of their husks, and bruised. Their pulpy substance, which seems to be the only part which constitutes the dye, is then put into a cistern, with just enough water to cover it, and in this situation it remains for seven or eight days, or until the liquor begins to ferment, which, however, may require as many weeks, according to circumstances. It is then strongly agitated with wooden paddles or beaters to promote the separation of the pulp from the seeds. This operation is continued until these have no longer any of the colouring matter adhering to them; it is then passed through a sieve, and afterwards boiled, the colouring matter being thrown to the surface in the form of scum, or otherwise allowed to subside: in either case it is boiled in coppers till reduced to a paste, when it is made up into cakes and dried." *

Another and more preferable mode of extracting the colouring matter from these seeds, is by rubbing them one against another under water, so that the mucilaginous and other impure matters contained in the interior of the seed are not mixed in it. The colouring matter is allowed to settle, the water drawn off, and the annotta left to dry. When prepared in this manner, it has a fatty feel, is very homogeneous, and of a deep-red colour, which changes to dark-brown by drying. It has no taste, but generally a disagreeable smell, when brought into commerce. This smell, however, is not natural, but is owing to stale urine having been added to it, in order to improve its colour, and keep it moist.

* Annales de Chemie, tome 47.

The Carribee Indians prepare the annotta, which they employ for painting their bodies, by smearing their hands with oil, and then rubbing the seeds until the pulp is separated under the form of a paste, which adheres to their fingers, and which they remove with a knife and dry in the sun.

Annotta of good quality is of a lively red colour when just taken from the seeds, and before it has undergone any change. It was found by Mr. John to contain the following ingredients:—

Colouring and resinous matters.....	28·0
Vegetable gluten.....	26·5
Lignine.....	20·0
Extractive colouring matter	20·0
Matter resembling gluten and extractive.....	4·0
Aromatic and acidulous matters.....	1.5
	100·0

Boiling water dissolves annotta, giving a thick decoction of a yellow colour. Alkalis form with it a white precipitate, giving the liquor a clear orange colour, which acids make redder.

Muriatic acid has no action upon annotta; chlorine destroys its colour. Nitric acid completely decomposes it, forming several compounds, which have not yet been sufficiently examined. Sulphuric acid poured upon solid annotta gives it a deep-blue colour, not unlike indigo, but it soon changes to a dark dirty-green, and then to a blackish-purple.

The colouring matters of annotta are easily soluble in alkalis, and in this condition they are generally used in the dye-house. The alkali used is either carbonate of soda or potash; and when light shades upon silks and fine cottons are wanted, soft soap is used. Sometimes a quantity of annotta is prepared and kept as a stock liquor; but the practice is bad, as the liquor soon becomes stale, and loses a great portion of its dyeing properties. It is best when newly prepared. A good method of preparation is the following:—Into a boiler, capable of containing 10 to 12 gallons of water, are put 10 pounds weight of annotta, 2 lbs. of carbonate of soda, and 2 lbs. of

soft soap, and the mixture is boiled until the annotta is all dissolved.

Cloth put into this solution is dyed a dark orange, but every shade, from an orange to a cream colour, can be dyed with it by merely using it in a proper state of dilution with water. The cloth requires no previous preparation; but for fine light shades the colour is improved by dissolving a little white soap in the water used for diluting it. The goods are merely passed through the solution, and dried from it; but where the colour is strong, the cloth must be washed in water containing a little soap, to free it from the strong alkali in the colouring solution. The addition of acids turns the colours of cloths dyed by annotta to a yellowish-red, so that by passing a piece of cloth dyed orange through water, slightly acidulated, it assumes a scarlet or salmon colour, according to the quantity of colouring matter used. But all the colours dyed by annotta are exceedingly fugitive, and although neither acids nor alkalis can completely remove the colours dyed by it, still they are constantly changing and fading by exposure to the air and light. On this account annotta is now very seldom used in the cotton dye-house, and then it is used only as an auxiliary. It is, however, still used for silks and woollens, as the objections to its use for cotton do not apply so strongly in its relations to those substances. It may also be used with propriety for mixed fabrics, such as silk and cotton, silk and woollen, &c.

Annotta was considered to contain two distinct colouring matters, a yellow and red, till it was shown by M. Preisser that the one is the oxide of the other, and that they may be obtained by adding a salt of lead to a solution of annotta, which precipitates the colouring matter. The lead is separated by sulphuretted hydrogen; and the substance being filtered and evaporated, the colouring matter is deposited in small crystals of a yellow-white colour. These crystals consist of *bixine*: they become yellow by exposure to the air, but by dissolving them in water this change is prevented.

Sulphuric acid gives...A yellow, which does not turn blue as it does with annotta.
Nitric acid .....A yellow shade.
Chromic acid.....A deep-orange tint.

When ammonia is added to bixine with free contact of air, there is formed a fine deep-red colour, like annotta, and a new substance is produced, termed *bixeine*, which does not crystallize, but may be obtained as a red powder; this is coloured blue by sulphuric acid, and combines with alkalis, and is *bixine* with addition of oxygen. When annotta, in the form of paste, is mixed from time to time with stale urine for its improvement, it is more than probable that this improvement consists in the formation of *bixeine* from the *bixine*, by the ammonia of the urine. This is rendered the more probable by finding the interior of the annotta yellow, while the red colour is much more developed upon the surface where the air has free access to it. This naturally suggests the mixing of annotta with a little ammonia, and exposing it to the air as much as possible previous to its being prepared for dyeing, as a much richer colour is thereby obtained.

The adulterations of annotta are oxide of lead and ochre. These may be detected by burning a small quantity of it in a china crucible: if pure, no residue will be left; but if oxide of lead be the adulterant, by keeping the crucible at a red heat, a small button of lead will be obtained; and if ochre be present, a red powder will be left.

The liquid sold in shops under the name of Scott's nankeen dye, is a solution of annotta and potash in water.

Annotta is often used for colouring butter and cheese.

Alkanet Root.

This is the root of a plant (*Lithos permum tinctorium*) which grows in the Levant and several other warm countries. It was introduced as a dye a few years ago, but with little success. The colouring matter is slightly soluble in water, but is rendered soluble by alkalis, to which it gives a blue colour, also by oils and fatty substances, which it colours red. It has the following reactions:—

Salts of lead	Blue precipitates.
Salts of tin	Crimson precipitates.
Salts of iron	Violet-colour precipitates.
Salts of alumina	Violet precipitates.

A variety of shades of lavender, lilac, violet, &c. are dyed by this colouring matter, but caution and experience are necessary to ensure success, and the colours obtained are easily affected by light—which, in our opinion, is the greatest barrier to its use. Colours formerly were generally dyed with it by giving the cloth an oil or soap preparation, the soap being combined with alumina to serve as the base.

Archil.

This colouring matter is prepared from lichens, a species of sea-weed. The most esteemed is that denominated *Lichen rocella.* The best sort comes from the Canary and Cape de Verde islands; but it is also found abundantly on the coast of Sweden, Scotland, Ireland, and Wales, and the people have from time immemorial used it for dyeing cloths. The colouring matters prepared from these lichens have been long known in commerce in the following forms:—

1st. As a pasty matter, called archil.
2d. A mass of a drier character, called persis; and,
3d. As a red powder, called cudbear.

The details of the mode of preparing archil have been kept a secret, and are but imperfectly known even yet. The following is what is known:—The lichens are first ground between two stones to a pulp, with the addition of water, and afterwards put into a wooden trough, having a tightly-fitted cover; upon the moist pulp is sprinkled a mixture of urine and ammonia, and the vessel being then covered, fermentation soon begins. The whole is occasionally stirred, and more ammonia and urine are added from time to time. After a few days, the colour begins to develop itself, but about six weeks are required to complete the operation. The whole is then removed from the trough and placed in casks, and may be kept for years. The keeping is considered to improve the intensity of the colour, which should be of a deep reddish-violet.

Acids change the colour to.....Bright red, and
Alkalis to.....A blue.

Sea-salt gives it.....A crimson tint.
Salammoniac.....A ruby-red tint.
Alum throws down.....A brownish-red precipitate.
Salts of tin.....Red precipitates.
Salts of iron.....Red-brown precipitates.
Salts of copper.....Cherry-brown precipitates.

There are no mordants required for dyeing with archil. It is not used for cotton dyeing, but extensively for silk and woollen, imparting very beautiful tints, which, however, are not permanent. It is often used as a bottom colour for reds which are to be dyed by safflower, cochineal, &c. and gives depth and a beautiful rich tint to the colours so dyed.

The colouring principle of these lichens, and especially that producing the archil, has been the subject of extensive investigation with some of the first chemists both in this and other countries. The results of these researches are, that the colouring matter of these lichens depends upon the oxidation of a colourless base, or compound existing in the plant. That of archil is termed orceine, and the oxidized colour is known as orcine. Dr. Stenhouse has given very simple methods of obtaining these matters from the lichens. Could this colour be obtained of a permanent character, and fixed upon cotton, its value would be inestimable.

PROPOSED NEW VEGETABLE DYES.

THERE are occasionally papers, of great value to the dyer, appearing in periodicals and the reports of scientific societies, that are not seen by practical men, and their value to a great extent is consequently lost. We have selected a few in proof of this statement, and trust it will stimulate to a more active research after such articles, which cannot fail to be productive of good results.

SOORANJEE.

This substance was investigated lately by Professor Anderson, from whose paper we give the following account:—

"The subject of these experiments was imported into Glasgow, some time since, under the name of Sooranjee, with the intention of introducing it as a substitute for madder in the art of dyeing. For this purpose it was, on its arrival, submitted for trial to some of the most experienced and skilful calico printers in Glasgow, all of whom concurred in declaring it not to be a dye at all, and to be totally destitute of useful applications. My friend, Professor Balfour, happening to hear of this circumstance, was so good as to obtain for me a quantity of the root, which has enabled me to submit it to a chemical investigation.

"Sooranjee is the root of the plant, and is imported cut up into pieces from one to four inches in length, and varying in diameter from half down to nearly an eighth of an inch. On the small pieces the bark is thick, and forms a large proportion of the whole root, but on the larger fragments it is much thinner. Its external colour is pale grayish-brown; but when broken across, it presents colours varying from fine yellow to brownish-red, and confined principally to the bark. The wood itself has only a slight yellowish shade, deepest in

the centre, and scarcely apparent close to the bark; but it is coloured dark red by alkalis, indicating the presence of a certain quantity of colouring matter in it. The bark is readily detached, and its inner surface, as well as that of the wood, has a peculiar silvery appearance, most apparent on the large pieces and almost entirely absent in the smaller. Boiled with water, it gives a wine-yellow decoction, and with alcohol a deep-red tincture.

"Solution of morindine gives with subacetate of lead a precipitate depositing itself in crimson flocks, which is extremely unstable, and cannot be washed without losing colouring matter. With solutions of baryta, strontia, and lime, it gives bulky-red precipitates, sparingly soluble in water. Perchloride of iron produces a dark-brown colour, but no precipitate. When its ammoniacal solution is added to that of alum, the alumina precipitated carries down with it the morindine as a reddish-lake; and when added to perchloride of iron, a brown precipitate is thrown down, which cannot be distinguished from pure peroxide of iron, but which contains morindine, as the supernatant fluid is colourless.

"The formula thus ascertained brings out an interesting relation between morindine and the colouring matters of madder, and more especially that one which is obtained by the sublimation of madder purple. From his analysis of this substance, Schiel * deduces the formula $C_7\ H_4\ O_4$. As this, however, is no more than the simplest expression of the analytical results, and as all the other madder-colouring matters examined contained 28 equivs. of carbon, we are justified in supposing its real constitution to be represented by quadruple of that formula, or $H_{28}\ H_{16}\ O_{16}$, which differs from that of morindine by a single equivalent of water only. The unsublimed madder purple is also connected, though more remotely, with morindine, and differs only by containing 5 equivs. of hydrogen less, its formula according to Schiel being $C_{28}\ H_{10}\ O_{15}$.

"This similarity, however, does not extend itself to their properties, as dyes, in which respect they differ in a very remarkable manner. I have already mentioned that the calico printers had entirely failed in producing a colour by means of sooranjee; and this I have fully confirmed as regards the common mordants. I digested morindine for a long time,

* Chemical Gazette, vol. v. p. 77.

in a gradually increasing heat, with small pieces of cloth mordanted with alumina and iron; but nothing attached itself, and the mordants, after boiling for a minute or two with soap, were found to be unchanged. Even with the root itself alum mordant only acquired a slight reddish-gray shade, and iron became scarcely appreciably darker in colour. The case was different, however, when cloth mordanted for Turkey red was employed. I obtained from Glasgow pieces of calico prepared for Turkey red both by the old and new processes; and I found that both acquired with morindine, in the course of a couple of hours, or even less, a dark brownish-red colour, devoid of beauty, but perfectly fixed. These observations agree with the account given by Mr. Hunter of the method of dyeing with the *M. citrifolia* employed by the Hindoos. The cloth is first soaked in an imperfect soap, made by mixing the oil of the *Sesamum orientale* with soda-ley. After rinsing and drying, it is treated with an infusion of myrobalans, (the astringent fruit of the *Terminalia chebula*,) and exposed for four or five days in the sun. It is then steeped in solution of alum, squeezed, and again exposed for four or five days. On the other hand the powdered roots of the *Morinda* are well rubbed with oil of sesamum, and mixed with the flowers of the *Lythrum fruticosum* (Roxburgh) or a corresponding quantity of *purwas*, (the nut-gall of a species of *Mimosa*.) The whole is introduced along with the cotton into a large quantity of water, and kept over a gentle fire for three hours, when the temperature is brought to the boiling point. The red colour so obtained is, according to Mr. Hunter, more prized for its durability than its beauty. This is simply a rude process of Turkey red dyeing. He also mentions that, by means of iron mordant, a lasting purple or chocolate is obtained; but in this case the colour is probably affected by the tannine of the astringent matters employed in the process.

"Morindine is a true colouring matter, and is capable of attaching itself to common mordants. It gives with alumina a deep rose-red, and with iron violet and black; but the colours are not very stable, and it has a strong tendency to attach itself to the unmordanted parts of the cloth and to degrade the white. Morindine, after treatment with sulphuric acid, is capable of attaching itself to ordinary mordants.

"The discovery of a peculiar colouring matter capable of

fixing itself exclusively on Turkey red mordant, is of interest as establishing the existence of a peculiar class of dyes hitherto totally unsuspected, a class which may be extensive, and may yield important substances. It may serve also in some respects to clear up the *rationale* of the process of Turkey red dyeing, which has long been a sort of opprobrium of chemistry. Although that process has been practised for a century in Europe, and has undergone a variety of improvements, no clear explanation of it was for a long time given; but it was supposed that, by the action of the dung, of which large quantities are employed, the cloth underwent a species of *animalisation*, as it was called, by which it acquired the property of receiving a finer and more brilliant colour than could be attached to it by purely mineral mordants. Recent experiments have, however, shown that the oil, which is largely employed in the process, undergoes decomposition by long exposure to the air in contact with decomposing animal matter, and is converted into a sort of resinous matter, which constitutes the real mordant for Turkey red. This has been pretty clearly made out by the experiments of Weissgerber.* He found that when cloth had been treated with oil, so as to give when dyed a fine rose-red colour, he could, by digestion with acetone, extract from it the altered oil; and as it was removed the cloth gradually lost the power of attracting the colouring matter of madder, until, when it was entirely separated, the cloth passed through the dye without acquiring any colour. On the other hand, he found that, by applying the substance extracted by acetone in sufficient quantity to cloth, he could obtain the richest and deepest colours with madder, without the addition of any other substance whatsoever. These observations receive additional confirmation from the experiments detailed in the present paper, as it must be sufficiently obvious that the dark-red colour obtained on Turkey red mordant with morindine must be entirely irrespective of the alumina, on which that substance is incapable of fixing.

"I fully agree with the opinion expressed by Persoz, that the use of alum mordant, which is at present always employed in Turkey red dyeing, will be entirely abandoned as soon as calico printers have learned the method of modifying at will

* Persoz, sur l'Impression des Tissus, vol. iii. p. 176.

the oil which they employ, so as to bring it at once into the state in which it acts as a mordant. Some steps have been made in this direction by making use of some chemical agents, as nitric acid and chloride of lime, for the purpose of acting on the oil; but the improvements which have been effected stop far short of what I believe will eventually be effected when the system of pure empiricism, which has been all along employed in this particular process of dyeing, is abandoned, and the subject submitted to really scientific investigation. It is understood that M. Chevreul has entered upon the inquiry, and in his hands there is little doubt but that it will meet with a satisfactory solution."—From the *Transactions of the Royal Society of Edinburgh.*

Carajuru or Chica

Is a vegetable substance known by these names, and is obtained from America, where it is used by the natives as a dye. The following short extracts from a paper by J. J. Virey, will show its character and properties:—

"M. de Humboldt has described in the 'Annales de Chemie et Physique,' (vol. xxvii. p. 315,) under the name of *Chica*, a vegetable product of a brick-red colour, obtained by macerating in water the leaves of *Bignonia chica*, a shrub of the family of the *Bignoniaceæ* from equinoctial America.

"As we have obtained from Para in Brazil, under the denomination *Crajuru* or *Carajuru*, a substance not only analogous in its physical and chemical characters to the *Chica*, but of a red-brown violet tint, much more beautiful and rich, and like vermilion, whilst the other appeared duller and much inferior, it may be useful to give fresh details about this product, which has been imported to be tried in dyeing.

"The *Crajuru* or *Carajuru* (*Carucuru* according to others) is a kind of powder or fecula, in pieces somewhat light, inodorous, insipid or slightly bitter, not soluble in water, but soluble in alcohol, ether, and the oils and fats, without being completely resinous, burning with a flame, but leaving a quantity of gray cinders. It is wholly dissolved by alkalis, and acids precipitate it without greatly altering its colour, if they are not concentrated.

"The *Crajuru* now brought into Europe must furnish a rather strong and beautiful dye, the brilliancy of which appears quite superior to that of orleans." *

WONGSHY

Is another vegetable substance. An investigation of its properties was made by W. Stein, from whose paper we extract the following account:—

"Towards the end of last year, a new material for dyeing yellow, called *wongshy*, was exported on experiment from Batavia to Hamburg, for a sample of which I am indebted to the kindness of M. Vollsack, merchant. Whether it has hitherto been applied as a dyeing material, and with what results, could not be ascertained. The following notice, therefore, will probably not be without interest:—

"The new dyeing material consists of the seed-vessels of a plant, which, according to the information from M. Reichenbach, belongs to the family of the Gentianeæ. The form of the unilocular capsules is longish-ovate, drawn out to a point next the end of the peduncle, and crowned upon the opposite and more obtuse one with the dried six-lobed calyx. They vary in size; but on an average their length is 1·5 to 2 inches, and the diameter at the thickest part 0·5; the colour is not uniformly reddish-yellow, but at some places darker, at others lighter. The surface is more or less irregularly waved with six to eight longitudinal ribs. The odour resembles saffron, and subsequently honey. The shell is pretty hard and brittle, but becomes quickly mucilaginous when chewed, imparting a yellow colour to the saliva, with a slightly bitter taste; it swells up considerably in water. Inside the capsules there are a number of dark reddish-yellow seeds (in one specimen I counted 108); they are not attached

* "The drink called *chica*, which is so much used among the people of South America, must not be confounded with the subject of the present notice. This drink, in fact, is prepared with pods of algaroba, (*Mimosa algaroba*,) which are nearly as sweet as the carouba of the *Ceratonia Siliqua*, and with the bitter stalks of the *Schinus molle*. It is said that old women are employed to chew these *Algarobæ* and the *Schinus*, and then to spit them into a vessel; water is added; the whole soon ferments, and affords a kind of intoxicating beer."

to the sides, but are imbedded in a hardened pulp, and so connected one with the other. These seeds are tolerably hard, soften but slowly when chewed, have no particular taste, but after some time produce at the point of the tongue a slight but peculiar sourish-sweet pungency, resembling the action of Paraguay rue. The pulp, on the other hand, cementing them together has a strong bitter taste, which is particularly perceptible at the back part of the palate.

"The wongshy, especially when pounded, readily gives up to water, both at the usual temperature as well as on boiling, a colouring principle which possesses such an enormous divisibility, that two parts of the pounded capsules furnish 128 parts of a liquid, which, placed in a cylindrical vessel of white glass with a diameter of three inches, still appears of a bright wine-yellow colour. The concentrated extract is very mucilaginous, and has a fiery-red colour, which, on large dilution, passes into a golden-yellow, the red disappearing.

"Protochloride of tin produces no change at the ordinary temperature, or after a long time; on boiling, a dark orange-coloured precipitate results.

"Acetate of lead produces no change.

"Basic acetate of lead causes a turbidness at the ordinary temperature, and an orange-coloured precipitate on boiling.

"Protosulphate of iron changes the colour into a dark brownish-yellow, without, however, a precipitate resulting either in the cold or on ebullition.

"Alum, acetate of alumina, and acetate of zinc, produce yellow precipitates only on boiling.

"Barytic water causes a yellow precipitate at the ordinary temperature, which on boiling acquires a reddish tint.

"Lime-water gave a pure yellow precipitate; solutions of gypsum and chloride of calcium are not precipitated by it even on boiling; well water, with a considerable amount of carbonate of lime, does not precipitate the colouring principle even with the assistance of heat; it is consequently not able to decompose the combinations of lime with acids.

"To ascertain the value of the wongshy colouring matter for the purposes of dyeing, 1 part of the pounded capsules was digested for twelve hours with 20 parts of lukewarm water, being frequently stirred, and the liquid then strained. The colouring matter is most quickly extracted in this manner

without its becoming gelatinous from the formation of paste, as would happen were the liquid boiled. Properly prepared samples of woollen cloth, some without any mordant, others mordanted with alum, protochloride of tin, acetate of alumina, and basic acetate of lead, were dyed with this extract at a temperature of about 104° Fah.; the colour does not turn out so pure at a higher temperature. The unmordanted cloth was dyed a beautiful and uniform orange colour by one immersion; of the mordanted samples, those with alum and acetate of alumina were better than those with protochloride of tin; the least satisfactory was that in which basic acetate of lead had been used as mordant. The tone of the colour was not altered by the three first mordants, but it was less intense, and the stuffs were not uniformly penetrated by the colouring matter. However, the samples with alum mordant gave perfectly satisfactory results after a second immersion. The colouring matter likewise combines readily and uniformly with silk, communicating to it a very glowing golden colour, so that in this case I also prefer not having recourse to mordants. Cotton, as was to be expected, can only be dyed with the assistance of mordants, and the best results appeared to be obtained with tin mordants; the colour was orange, of a very agreeable tint.

"The colour, both upon wool, silk, and cotton, resists soap perfectly; but alkalis give it a yellow, acids and tin salt a red tint. By this behaviour it differs from the colour of annotta, with which, as will subsequently be seen, it possesses in other respects great resemblance, a resemblance which unfortunately exists as regards the action of light. When exposed to light, the colour very soon fades upon cotton, less quickly upon wool; and in this case it is more permanent upon the unmordanted samples. It resists the light longest upon silk; and, in this respect, when compared with the other known yellow colours, may be reckoned among the best.

"I obtained a beautiful yellow, with a faint tint of red, by mordanting the woollen cloth with lime-water, and immersion in the boiling vat; it resists the soap perfectly, and the action of light much better than the orange. It is altered in a similar manner to the orange by alkalis, acids, and tin salt, only less. Several very beautiful shades of yellow may be obtained by

adding pearlash or caustic potash to the dye, and immersing the unmordanted fabric at the ordinary temperature. The union of the colour with the fibre takes place very quickly and very uniformly. By the addition of 1 part pearlash to 30 parts dye liquor, a yellow was obtained with a remarkable glow from a slight admixture of red. By the addition of twice the quantity of pearlash, a lively yellow, with a faint tint of green, was obtained. A still larger amount of pearlash cannot be used, as it renders the colour dull and impure. With caustic potash, instead of pearlash, I obtained, in the first place, a pure brilliant yellow, with less red than with the pearlash; in the latter case, a beautiful canary-yellow with a shade of green. Ammonia acts in the same manner, but the colour, under all circumstances, contains more red. The colour also appears of a somewhat different shade when the fabrics are first immersed in the dye liquor, and then, after being washed, placed in an alkaline bath.

"In the case of silk and cotton, the effect of alkalis is similar, but less apparent, because the silk and cotton fibres imbibe less of the colouring substance than those of wool.

"That this colour resists the soap is self-evident, but it also suffers less from the action of light than the orange; and when fabrics so dyed are passed through a vinegar or muriatic acid bath, a brilliant aurora colour is obtained. This interesting behaviour, which the wongshy colouring matter has in common with that of annotta, is explained by the chemical character of the former, which is a weak acid; it combines with the alkalis and with the alkaline earths, as evident by the precipitation with baryta and lime-water. Its combinations with the former possess a pure yellow colour, and are decomposed by stronger acids, when the liberated colouring matter separates of a brilliant vermilion colour. But the colouring matter thus separated is no longer the same as that which was originally contained in the aqueous solution, for it is now perfectly insoluble in water, and is only dissolved in small quantity, and of a golden-yellow colour, by absolute alcohol, ether, and spirit of 0·863 spec. grav. In the moist state it has a vermilion colour; when dry and in the purest state, it is brown-red, like Ratanhia extract, and is easily reduced to powder; but if it still contains sugar and fat, it has a beautiful yellowish-red colour, in thick layers, whilst in thin layers

it is yellow and transparent, and becomes moist in the air. On heating the pure substance upon platinum, at first yellow vapour is given off, and at some spots the colour becomes pure yellow; it subsequently turns black, fuses, and chars. The residual cinder is difficult to burn; the yellow vapours condense, when the experiment is made in a glass tube, into yellow oily drops. Concentrated sulphuric acid renders it scarcely perceptibly blue, and the acid acquires the same colour, which quickly passes into violet and brownish-red, whilst the colouring matter slowly dissolves. Water separates from this solution a dirty yellowish-gray flocculent substance.

"The reaction of the wongshy colouring matter which has just been mentioned, has no resemblance with the reaction of sulphuric acid upon annatto, for the liquid never acquires a pure blue colour, as is the case with annatto, but is violet from the first, and only for a minute.

"It dissolves readily in caustic ammonia and caustic soda, with a golden-yellow colour."

ALOES.

Dr. Bancroft in his work on the Philosophy of Permanent Colours, recommended this substance as a dyeing agent. He proposed to digest it in nitric acid, by which means he obtained alœtic acid, a substance capable of being used as a dye. This matter has been the subject of extensive investigation by many chemists, and has been occasionally more or less used as a dyeing agent. A patent, however, has recently been taken out for certain applications of aloes to dyeing. The following is the proposed method of preparation:—

"The mode of preparing the colouring matter from aloes is as follows:—Into a boiler or vessel, capable of holding about 100 gallons, the patentee puts 10 gallons of water, and 132 lbs. of aloes, and heats the same until the aloes are dissolved; he then adds 80 lbs. of nitric or nitrous acid, in small portions at a time, to prevent the disengagement of such a quantity of nitrous gas as would throw part of the contents out of the boiler. When the whole of the acid has been introduced,

and the disengagement of gas has ceased, 10 lbs. of liquid caustic soda, or potash of commerce, of about 30° are added, to neutralize any undecomposed acid remaining in the mixture, and to facilitate the use of the mixture in dyeing and printing. If the colouring matter is required to be in a dry state, the mixture may be incorporated with 100 lbs. of China clay, and dried in stoves, or by means of a current of air. In preparing the colouring matter from extract of logwood, the materials are used in the manner and proportions above described; the only difference being, that the extract of logwood is substituted for the aloes.

"The colouring matter is used in dyeing by dissolving a sufficient quantity in water, according to the shade required, and adding as much hydrochloric acid or tartar of commerce as will neutralize the alkali contained in the mixture, and leave the dye-bath slightly acidulated. The article to be dyed is introduced into the bath, which is kept boiling until the desired shade is obtained.

"When the colouring matter is to be used in printing, a sufficient quantity is to be dissolved in water, according to the shade required to be produced; this solution is to be thickened with gum, or other common thickening agent; and hydrochloric acid, or tartar of commerce, or any other suitable supersalt is to be added thereto, for the purpose before mentioned. After the fabrics have been printed with the colouring matter, they should be subjected to the ordinary process of steaming, to fix the colour."—Sealed Jan. 27, 1847.

Pittacal.

This substance is obtained from beech tar. It is dry and hard, very brittle, and resembles indigo in appearance. It has no taste or smell, and does not dissolve in water. Sulphuric acid dissolves it, producing a violet-coloured solution. Muriatic acid gives a red-purple solution, from which alkalis precipitate the pittacal. Acetate of lead, salts of tin, sulphate of copper, acetate of alumina, all give deep-blue precipitates, not readily changed. This colour is fixed easily upon cotton by tin and alumina.*

* Records of General Science.

Barbary Root.

The plant from which this is obtained grows in almost every part of the world; great quantities of it are obtained from India, where it grows in great abundance and perfection. The colouring matter is found in the whole of the root. In the stem it is found round the pith and near the bark. This colouring substance is much used in dyeing or staining leather; but it is not much used in dyeing of cotton. Mr. Edward Solly has made some investigations of this root. See Journal of the Royal Asiatic Society.

ANIMAL MATTERS

USED IN DYEING.

THE colouring substances remaining to be noticed belong to the animal kingdom. They are but few in number, and none of them as yet made suitable for dyeing on cotton.

COCHINEAL.

This is a small insect called the *coccus cacti*, and is much sought after for its tinctorial qualities. It furnishes the finest known shades of crimson, red, purple, scarlet, &c. for woollen and silk. The insects are reared in great abundance in Mexico. They feed upon a cactus plant, which the natives cultivate round their dwellings for that purpose. The insects attach themselves to the leaves of the plant, and increase rapidly in number. The females live about two months, and the males only about one month. The season of rearing and gathering lasts about seven months: during this period the insects are gathered three times. After each gathering some of the branches and leaves containing females and their young, are preserved under shelter, and on the return of the proper season they are distributed over the plantation. A few females are put into a small nest made of some downy substance, and the young insects quickly spread themselves out upon the leaves, to which they attach themselves. They are gathered by brushing them off the leaves with the feather end of a quill into boiling hot water, in which they are kept a few seconds. This not only kills them instantly, but causes them to swell to twice their natural size. When taken out the hot water, they are spread out and dried, and then packed for the market. Some cultivators instead of hot water use steam, and others again place them in an oven or upon a hot plate. The difference in the appearance of the cochineal, is caused by these different modes of killing the insects and

heating them. They shrivel in drying, and assume the appearance of irregular formed grains, fluted and concave. The best sort seem as if dusted with a white powder, and are of a slate-gray colour; but these appearances are often imparted by means of powdered talc, to deceive the purchaser.

There are three kinds of cochineal in commerce. The finest is known by the name of *mistic*, from the name of the place in which the insects are reared, La Mistica, in the province of Honduras. Another is called *wild*, because they are collected from plants growing in a state of nature; but this variety is inferior to the former. The third is a mixture of these two, or rather the debris or fragments, and varies in quality according to the proportion of the mixture.

Cochineal has been the subject of several chemical investigations, the results of which are not very satisfactory. The following are instances of these. The cochineal contains—

1. Carmine, which may be termed the colouring matter.
2. A peculiar animal matter.
3. A fatty matter, composed of ..... { Stearine, Bleine, and Volatile fatty acids.
4. Saline matters, as ..... { Phosphate of lime. Carbonate of lime. Chloride potassium. Phosphate of potash. Combination of potash with organic acids.

Mr. John gives the following as the result of his analysis:—

Red-colouring matter	50·0
Gelatine	10·5
Wax	10·0
Debris of skin, &c.	14·0
Gummy matter	13·0
Phosphate of lime, of potash, and iron, and chloride potassium	14·0

Carmine, or the colouring matter of cochineal, may be obtained by macerating finely ground cochineal with ether, which dissolves out the fatty matter, and then dissolving the

carmine by the application of hot alcohol, and leaving the solution to cool: by evaporating, the carmine is deposited as a beautiful red crystalline substance, which dissolves freely in water. It is affected by the following re-agents as under:—

Tannin	Gives no precipitate.
Most acids	Change its colour from a bright to a yellowish-red.
Boracic acid	Does not change the colour, but rather reddens it more.
Potash, soda, and ammonia	Change it to a crimson-violet.
Baryta and strontia	Produce the same effect.
Lime	Gives a crimson-violet *precipitate.*
Alumina	Combines with it and precipitates it as a beautiful red; but if boiled it passes to violet-red. A little potash, soda, or ammonia added prevents this change, and preserves the stability of the red.
Protoxides of tin	Change it to crimson-violet.
Peroxide of tin	Changes it to yellowish-red.
Salts of iron	Turn it brown; no precipitate.
Salts of lead	Change it to violet; no precipitate.
Salts of copper	Change it to violet; no precipitate.
Nitrate of mercury	Gives a scarlet-red precipitate.
Nitrate of silver	Has no action upon it.
Chlorine	Turns it yellow.

"As may be supposed, the result of all these contrary opinions is, that it is perfectly impossible to judge of the goodness of a cochineal by its physical characters. In order to ascertain its value, we must have recourse to comparative experiments. We are indebted to MM. Robiquet and Anthon for two methods of determining the quality of cochineals, according to

the quantity of carmine they contain. The process of M. Robiquet consists in decolourizing equal volumes of decoction of different cochineals by chlorine. By using a graduated tube, the quality of the cochineal is judged of by the quantity of chlorine employed for decolourizing the decoction. The process of M. Anthon is founded on the property which the hydrate of alumina possesses of precipitating the carmine from the decoction so as to decolourize it entirely. The first process, which is very good in the hands of a skilful chemist, does not appear to us to be a convenient method for the consumer: in the first place, it is difficult to procure perfectly identical solutions; in the next place, it is impossible to keep them a long time without alteration. We know that chlorine dissolved in water reacts, even in diffused light, on this liquid, decomposes it, appropriates its elements, and gives rise to some compounds which possess an action quite different from that of the chlorine solution in its primitive state. The second process seems to us to be preferable, as the proof liquor may be kept a long while without alteration. A graduated tube is also used; each division represents one-hundredth of the colouring matter. Thus, the quantity of proof liquor added exactly represents the quantity in hundredths of colouring matter contained in the decoction of cochineal which has been submitted to examination.

"The colouring matter of cochineal being soluble in water, I have used this solvent for exhausting the different kinds which I have submitted to examination in the colourimeter. I operated in the following manner:—I took a grain of each of the cochineals to be tried, dried at 122° Fah.; I submitted them five consecutive times to the action of 200 grains of distilled water at water-bath heat, each time for an hour; for every 200 grains of distilled water I added two drops of a concentrated solution of acid sulphate of alumina and of potash. This addition is necessary to obtain the decoctions of the different cochineals exactly of the same tint in order to be able to compare the intensity of the tints in the colourimeter.*

* Care must be taken not to add to the water, which serves to extract the colouring matter from the different cochineals, more than the requisite quantity of acid sulphate of alumina and solution of potash, because a stronger dose would precipitate a part of the colouring matter in the state of lake.

"In order to estimate a cochineal in the colourimeter, two solutions obtained, as described above, are taken; some of these solutions are introduced into the colourimetric tubes as far as zero of the scale, which is equivalent to 100 parts of the superior scale; these tubes are placed in the box, and the tint of the liquids enclosed is compared by looking at the two tubes through the eye-hole, the box being placed so that the light falls exactly on the extremity where the tubes are. If a difference of tint is observed between the two liquors, water is added to the darkest (which is always that of the cochineal taken as type) until the tubes appear of the same tint.* The number of parts of liquor which are contained in the tube to which water has been added is then read off; this number, compared with the volume of the liquor contained in the other tube, a volume which has not been changed, and is equal to 100, indicates the relation between the colouring power and the relative quality of the two cochineals. And if, for example, 60 parts of water must be added to the liquor of good cochineal, to bring it to the same tint as the other, the relation of volume of the liquids contained in the tubes will be in this case as 160 is to 100, and the relative quality of the cochineals will be represented by the same relation, since the quality of the samples tried is in proportion to their colouring power."

Some of the German chemists, supposing that the plant upon which the insect feeds, might be the source of the colouring matter, instituted a series of experiments to determine that point, but without success. The conclusions they came to are, that the animal economy plays a prominent part in the formation of the colouring matter.

Carmine is manufactured extensively in France, and is used for superior red inks, paints, and for colouring artificial flowers. It is prepared on the large scale by boiling a quantity of cochineal in water with soda, and then adding to it a little alum, cream of tartar, and the white of eggs, or isinglass —which separates the carmine as a fine flaky precipitate. This precipitate is carefully collected.

* For diluting the liquors the same water must always be used which has served to extract the colouring matter of the cochineals under examination, otherwise the darkest decoction would pass into violet as water was added to it to bring back the tint to the same degree of intensity as that of the decoction to which it is compared.

There is something in the production of good carmine which is not yet fully understood. It has not yet been prepared in this country in the same perfection as in France, (page 16.) It is found also, that, with a coal fire, a smaller quantity of it is produced than when a wood fire is employed; and there are many other little points which show the delicacy of its preparation.

The residue of the carmine, and some portions of the precipitate from the cochineal, when first taken from the fire, are collected and boiled in water; to this mixture is added a solution of alum and chloride of tin, by which a beautiful red-coloured precipitate or lake is formed. This constitutes the beautiful pigment known as *carmine lake.*

Lake Lake, or Lac,

Is a concrete juice which distils from several kinds of plants. It appears, however, to be determined that it is caused by an insect named *coccus ficus*, or *cœcus loco*, and may therefore be regarded as of animal origin. There are several varieties of this product under the names of *stick lac*, *seed lac*, and *shell lac*. There is also brought from India two other products distinguished as *lac lac* and *lac dye*—which are the kinds mostly used in dyeing, but their composition is not very well known. They, however, contain a goodly quantity of resinous matter, which must be destroyed before they are put to use as a dye. *Lac lac* is obtained fit to use as a dye by boiling the gum lac with alkaline water, which dissolves the colouring matter along with some of the resinous. To this is added some alum, which precipitates the whole as an aluminous product, in which state it is used.

Dr. Bancroft discovered that acids destroyed the resinous matter of lac dye, and rendered the colouring matter soluble, and this is the mode generally adopted in working with this substance.

The following may be taken as the ordinary means of producing this colour:—Add to four pounds of lac dye, three pounds of strong sulphuric acid, and set the mixture aside for two days; pour over it half-a-gallon of boiling water; stir the whole well, and leave it to settle for twenty-four hours; the

clear liquor is then to be decanted into a leaden vessel, and the residue washed with water until all the colouring matter is dissolved. The washings may be added to the liquor in the leaden vessel. There is then added to this liquor a quantity of lime-water, until the solution barely tastes acid, which precipitates the sulphuric acid; the whole is then thrown upon a filter, and the clear liquor passing through the filter forms the dye.

Some dyers take about 32 parts of lac dye, and rub it down fine in 10 parts of strong sulphuric acid; then add three times the quantity of the mixture of water, and set aside for two days; it is then ready for use, requiring merely to be diluted as required.

The French dyers generally take 32 parts of lac dye, rubbed down in 12 parts of hydrochloric acid of 30° Twaddell; when well mixed, it is diluted with about an equal quantity of water, set aside for twenty-four hours, and stirred from time to time; it is then ready for use. Many dyers treat the lac lac in the same way as the lac dye, using one pound of sulphuric acid to two pounds of lac lac; in other respects the process is the same.

The mordants employed for dyeing with the lacs are termed *lac spirits;* the lac and spirits are mixed previous to using. *Lacs* are employed as substitutes for cochineal, and most of the colours obtained by the one are producible by the other; but for fine reds the lac is much inferior. This dye is only used for silk and woollen.

Kerms.

This is also an animal substance — the dried bodies of another species of the *coccus* insect. This insect is supposed to have been known as a dye so early as the time of Moses; it was used in India at a very early age, and was highly valued both by the Romans and Spaniards for dyeing purples; but after the cochineal dye was discovered, it was used in preference, on account of the superior beauty of the colours. Accordingly, in many countries where the kerms insect was reared and enriched the people, the remembrance of it is lost.

Good kerms is of a full deep-red colour, having a pleasant smell, and sharp sour taste; the red-colouring matter is soluble in water and in alcohol. It possesses properties similar to cochineal.

Acids render it	Yellowish-brown.
Alkalis	Crimson-violet.
Iron salts turn it	Black.
Alum renders it	Blood-red.
Salts of tin	A bright red.
A mixture of iron salts and tartar turns it to	Gray colour.
Sulphate of copper and tartar	Olive-green.
Tin salts and tartar	Cinnamon-brown.

For a red with tin it requires about 12 times the quantity of kerms as of cochineal, and the colour is a little inferior. As a dye, it is not much used, and only for silk or woollen. There is no affinity between cotton and the colouring matters of *cochineal*, *lacs*, and *kerms*.

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GLOSSARY OF TECHNICAL TERMS

USED IN THE DYE-HOUSE

WITH THE CHEMICAL NAMES:

A FULL EXPLANATION OF WHICH MAY BE OBTAINED IN THE VOLUME.

Adjective. A term applied to a colour depending on a base for its production.
Aqua-fortis. Nitric acid.
Aqua-regia. A mixture of hydrochloric and nitric acids, generally in the proportion of 2 of the former to 1 of the latter.
Alkali root. Alkanet root.
Alterant. A substance added to a colour to give it brightness, same as "raising."
Argol. Bitartrate of potash, formed by deposite on wine casks.
Arnotto. Annotta.
Barilla. The name of an impure soda imported from Spain and the Levant.
Black ash. Carbonate of potash in fused masses, as imported.
Black lead. Carburet of iron.
Black iron liquor. Acetate of iron, or pyrolignite of iron.
Bleed. To extract the colouring matter from a dye drug.
Bleaching powder. Chloride of lime.
Block tin. Commercial tin cast into ingots or blocks, not so pure as grain tin.
Borax. Borate of soda.
Blue copperas. Sulphate of copper.
Blue-stone. Sulphate of copper.
Blue vitriol. Sulphate of copper.
Bottom. Applied to the base of a colour such as sumach, galls, &c.
Brimstone. Sulphur.
Brown sugar. Acetate of lead, or pyrolignite of lead.

Bucking. Boiling goods in alkalis.
Bundle. Ten pounds of cotton yarn.
Calomel. Protochloride of mercury.
Carmine. Colouring matter of cochineal, extracted and dried.
Chamber ley. Urine.
Chemic, or chemic blue. Sulphate of indigo.
Chrome. Bichromate of potash.
Common salt. Chloride of sodium.
Copperas. Protosulphate of iron.
Corrosive sublimate. Bichloride of mercury.
Cream of tartar. Bitartrate of potash, purified. *See* argol.
Crofting. Exposing goods upon the grass for bleaching.
Crude tartar. *See* argol.
Dip. Generally applied to immersing goods in the blue vat.
Doctored. To adulterate, generally applied to giving an appearance of strong colour to dyewoods, by adding water to them.
Double muriate of tin. Bichloride of tin.
Epsom salts. Sulphate of magnesia.
Essential salt of lemons. Binoxalate of potash.
Extract of indigo. Sulphate of indigo.
Fast colour. Permanent colour.
Fancy colour. Colours subject to fade, fugitive.
Feathering. To granulate a metal.
Firing spirits. When tin by dissolving too rapidly or by heat, becomes converted into a bichloride.
Fluery of a vat. The froth of oxidized indigo floating on the surface of a blue vat.
Flowers of zinc. Oxide of zinc.
French tub. Protochloride of tin and logwood, plumb tub.
Glauber salts. Sulphate of soda.
Grain tin. Metallic tin in prismatic pieces.
Green vitriol. Sulphate of iron, copperas.
Hartshorn. Ammonia.
Kelp. Ashes left on burning sea weed.
Killing. Dissolving any substance in an acid, as iron in nitric acid, killing iron.
King's yellow. Sulphuret of arsenic.
Lactine. A curd of milk used for animalizing cotton.
Lemon juice. Citric acid.
Ley. Solution of an alkali, as potash or soda.
Lime shell. Caustic lime.
Lime stone. Carbonate of lime.
Litharge. Protoxide of lead.
Lunar caustic. Nitrate of silver.
Magnesia nigra. Manganese.
Marine acid. Hydrochloric acid.

Mineral alkali. Soda.
Mordant. Generally applied only to acetate of alumina.
Muriatic acid. Hydrochloric acid.
Muriates. Chlorides.
Nitromuriate of tin. A solution of tin in nitric and hydrochloric acids, forming a persalt.
Nitre. Nitrate of potash.
Oxymuriate of tin. Perchloride of tin.
Oxymuriate of potash. Chlorate of potash.
Oxymuriatic acid. Chlorine.
Oil of vitriol. Sulphuric acid.
Orpiment. Sulphuret of arsenic.
Oxygen of the bleachers. Chlorine, chloride of lime, bleaching powder.
Pearlash. Carbonate of potash.
Permuriate of tin. Perchloride of tin.
Prussiate of potash. Ferrocyanide of potassium.
Queen-wood. Brazil-wood.
Quicksilver. Mercury.
Raising. See alterant.
Realgar. Sulphuret of arsenic.
Red chrome. Bichromate of potash.
Red liquor. Acetate of alumina.
Rot steep. Steeping cloth in old leys to soften the paste, fermentation takes place, hence the name.
Roman vitriol. Sulphate of copper.
Saddening. Making a colour darker by means of a salt of iron.
Salammoniac. Chloride of ammonium.
Sali nixon. Bisulphate of potash.
Sal prunella. Fused nitrate of potash cast into balls, or cakes.
Sal volatile. Sesquicarbonate of ammonia.
Salt of lemons. Citric acid.
Salt of saturn. Acetate of lead.
Salt of soda. Carbonate of soda.
Salt of sorrel. Binoxalate of potash.
Salt of tartar. Carbonate of potash.
Salt of vitriol. Sulphate of zinc.
Salt perlate. Phosphate of soda.
Saltpetre. Nitrate of potash.
Salt sedative. Boracic acid.
Salts of tin. Crystallized protochloride of tin.
Salt cake. Sulphate of soda.
Saxon blue. Sulphate of indigo.
Scalding. Extracting a colouring matter by boiling water.
Smalt blue. Ground glass, made of alumina, silica, potash, or soda, coloured blue by oxide of cobalt.
Slaked lime. Hydrate of lime.

Sludge. Sediment of the blue vat.
Single muriate of tin. Protochloride of tin.
Sour. Water made acid by sulphuric acid.
Soda ash. Carbonate of soda.
Spirits. Solutions of chlorides of tin.
Spirits of salt. Hydrochloric acid.
Spirits of hartshorn. Ammonia.
Spirits of wine. Alcohol.
Spent. Exhausted of colour.
Stoveing. Hanging goods in the stove to dry.
Stock tub. Vessel filled with strong solution of a substance to be kept for use.
Sugar of lead. Acetate of lead.
Substantive colour. A colour fixed in the fibre without base or compound.
Supertartrate of potash. *See* argol.
Sweeten. To pour water upon goods, from a sour, as a partial wash.
Tartar. *See* argol.
Test blue. Sulphate of indigo.
Tincal. Borate of soda, borax.
Turnbull's blue. Ferrocyanide of iron, Prussian blue.
Vegetable alkali. Potash.
Verdigris. Acetate of copper.
Verditer. Acetate of copper.
Vinegar. Acetic acid.
Vitriol. Sulphuric acid.
Volatile alkali. Ammonia.
White vitriol. Sulphate of zinc.
White copperas. Sulphate of zinc.
White lead. Carbonate of lead.
Whiting. Carbonate of lime.
White zinc. Oxide of zinc.

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